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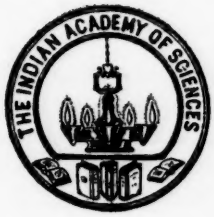

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EVALUATION OF THE ELASTIC CONSTANTS OF DIAMOND FROM ITS RAMAN FREQUENCIES

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1. Introduction

The frequencies of the normal modes of vibration of the structure of diamond admit of very precise determination from its Raman spectrum. According to the theoretical formulation of the dynamics of crystal lattices by Sir C. V. Raman (1943), a crystal with p atoms in its unit cell is capable of $(24p-3)$ normal modes of vibration. In the case of diamond, the vibration spectrum consists of eight discrete monochromatic frequencies of which one is triply degenerate, two are fourfold degenerate, three are sixfold degenerate and two are eightfold degenerate. The triply degenerate oscillation is active in the first order and manifests itself as a single very sharp and intense frequency shift of 1332 cm.$^{-1}$ (C. Ramaswamy, 1930). The remaining seven frequencies are inactive in the first order, but may be expected to manifest themselves as octaves and combinations in the second order Raman spectrum.

The investigations of R. S. Krishnan (1947) have shown that this is actually the case and that the octaves and combinations of the frequencies manifest themselves as sharply defined frequency shifts capable of being measured with high accuracy. A rigorous method of calculating the eight fundamental frequencies of the diamond lattice taking into consideration the interactions between each atom and its 28 nearest neighbours has been developed by K. G. Ramanathan (1947). The identification of the spectroscopic frequencies actually observed with the respective modes to which they refer presents no difficulty, since the eight frequencies arrange themselves in the correct order even in the first approximation where only the four nearest neighbours alone are considered. The identification is further confirmed by a consideration of the intensity relations between the different lines in the second order spectrum (C. V. Raman, 1947). Ramanathan's formulæ show that the eight fundamental frequencies are expressible in terms of eight force constants. The latter can therefore be completely evaluated.

The object of the present paper is a rigorous treatment of the problem of the evaluation of the three elastic constants of diamond, taking into account the interaction between each atom and its 28 nearest neighbours. Utilising the values for the force constants derived from K. G. Ramanathan's investigation of the second-order Raman spectrum, it is shown to be possible to determine the elastic constants from the spectroscopic data alone. A gratifying measure of agreement with the experimental values of the elastic constants emerges (Bhagavantam and Bhimasenachar, 1946).

2. The Energy of Deformation

The deformation energy can be represented as the sum of the changes in mutual energy of pairs of points. The strain energy W can be calculated in terms of the force constants and the relative displacements u, v, w of an atom i with respect to the atom o at the origin. The force components are:

$$\left.\begin{aligned} \mathrm{F}_x &= u\,\mathrm{F}_{xi}^{xo} + v\,\mathrm{F}_{yi}^{xo} + w\,\mathrm{F}_{zi}^{xo} \\ \mathrm{F}_y &= u\,\mathrm{F}_{xi}^{yo} + v\,\mathrm{F}_{yi}^{yo} + w\,\mathrm{F}_{zi}^{yo} \\ \mathrm{F}_z &= u\,\mathrm{F}_{xi}^{zo} + v\,\mathrm{F}_{yi}^{zo} + w\,\mathrm{F}_{zi}^{zo} \end{aligned}\right\}, \tag{1}$$

where F_{yi}^{zo} represents the force constant acting in the z direction on atom o due to the displacement of the atom i along the y direction. Hence the deformation energy for this pair is given by

$$\phi_i = -\tfrac{1}{2}\,[u\,\mathrm{F}_x + v\,\mathrm{F}_y + w\,\mathrm{F}_z]. \tag{2}$$

The relative displacement of the atom i is made up of two parts. The first part consists of the relative displacement of the two interpenetrating lattices with respect to each other. The second part consists of a uniform expansion or contraction along the three directions which is the same for both lattices. Hence u, v, w are given by

$$\left.\begin{aligned} u &= k_x + \left(x_i \frac{\partial u}{\partial x} + y_i \frac{\partial u}{\partial y} + z_i \frac{\partial u}{\partial z}\right) \\ v &= k_y + \left(x_i \frac{\partial v}{\partial x} + y_i \frac{\partial v}{\partial y} + z_i \frac{\partial v}{\partial z}\right) \\ w &= k_z + \left(x_i \frac{\partial w}{\partial x} + y_i \frac{\partial w}{\partial y} + z_i \frac{\partial w}{\partial z}\right) \end{aligned}\right\} \tag{3}$$

where k_x, k_y, k_z represent the relative inner displacement between the two atoms. In the case of a pair of points belonging to the same lattice $k_x = k_y = k_z = 0$. x_i, y_i, z_i represent the position of the atom i in the undeformed state. The terms $\frac{\partial u}{\partial y}$, $\frac{\partial v}{\partial x}$, etc., are the components of a tensor

which can be presumed to be symmetrical since a simple rotation is of no significance.

We may remark that the displacements u, v, w increase proportionately with the distance of the atoms from the origin and the number of such atoms to be taken into account increases even more rapidly at the same time. Hence even if the force constants diminish rapidly with increasing distance —as they should—the expression for the deformation energy may be expected to converge rather slowly. The numerical values for the force constants deduced by Ramanathan fall off very quickly with increasing distance. Even so, as we shall see, the outermost 12 of the 28 neighbours considered by him play a far from negligible role in determining the magnitude of the elastic constants of diamond.

3. The Force Constants

The force constants introduced by Ramanathan can be defined by using the notation given above.

$$P = F^{xo}_{xo} = F^{yo}_{yo} = F^{zo}_{zo}$$

$$Q = F^{xo}_{xi} = F^{yo}_{yi} = F^{zo}_{zi}$$

$$R = F^{xo}_{yi} = F^{xo}_{zi} = F^{yo}_{xi} = F^{yo}_{zi} = F^{zo}_{xi} = F^{zo}_{yi},$$

where i represents the atom at (1, 1, 1). The unit used for coordinates is $d/4$, where d is the lattice constant $= 3{\cdot}56$ A.U.

For the second neighbours we have

$$S = F^{xo}_{xi}; \quad T = F^{xo}_{yi} = F^{zo}_{zi}$$

$$U = F^{yo}_{yi} = F^{zo}_{zi}$$

$$V = F^{yo}_{zi} = F^{zo}_{xi} \text{ and } W = F^{yo}_{xi} = F^{zo}_{yi},$$

where i represents the atom at (0, 2, 2).

For the third neighbours we have

$$\alpha = F^{xo}_{xi} = F^{zo}_{zi}$$

$$\beta = F^{xo}_{yi} = F^{zo}_{yi}$$

$$\gamma = F^{xo}_{zi} = F^{zo}_{xi}$$

$$\delta = F^{yo}_{yi} \text{ and } \epsilon = F^{yo}_{xi} = F^{yo}_{zi},$$

where i represents the atom at (1, -3, 1).

Due to the symmetry of the structure of diamond, the force constants for the other atoms can be got by considering the position of the atom and the

nature of its displacement. The actual constant involved in a particular case can be found from the table given by Ramanathan.

In the case of second neighbours, there is a plane of reflection perpendicular to the *yz* plane bisecting the line joining the origin to the atom (0, 2, 2) and hence it can be shown that $T = -V$.

In the case of third neighbours, there is a centre of inversion between the two atoms which involve the constants β and ϵ. By inverting about the centre it can be proved that $\beta = \epsilon$. These two relations considerably simplify the calculations.

4. Elimination of the Inner Displacements

In the deformed state each lattice point should be in equilibrium. Due to the relative displacement of each of the 28 surrounding neighbours, forces act on the atom at the origin. These forces should be in equilibrium. The relative displacement of each atom is known from equation (3), and the forces can be computed from equation (1) by substituting the proper force constants. In the summation of the forces due to all the atoms it is found that the effect of the second neighbours add up to zero. Due to the symmetry of the crystal, the final expression gets considerably simplified and we have

$$k_x \{4Q + 8a + 4\delta\} + \left\{\frac{\partial v}{\partial z} + \frac{\partial w}{\partial y}\right\} (4R + 8\beta - 12\gamma) = 0$$

i.e.,
$$k_x (Q + 3\Sigma) + \left\{\frac{\partial v}{\partial z} + \frac{\partial w}{\partial y}\right\} (R + 2\beta - 3\gamma) = 0,$$

where $3\Sigma = 2a + \delta$,

Hence
$$k_x = -\frac{(R + 2\beta - 3\gamma)}{(Q + 3\Sigma)} \left(\frac{\partial v}{\partial z} + \frac{\partial w}{\partial y}\right)$$

$$k_y = -\frac{(R + 2\beta - 3\gamma)}{(Q + 3\Sigma)} \left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x}\right)$$

$$k_z = -\frac{(R + 2\beta - 3\gamma)}{(Q + 3\Sigma)} \left(\frac{\partial v}{\partial x} + \frac{\partial u}{\partial y}\right)$$

It is important to remark that the inner displacements are of considerable magnitude and that the equilibrium condition is not satisfied if we assume that the inner displacements do not exist.

5. Calculation of the Deformation Energy

The deformation energy of the 28 typical pairs of points can be written down and the final summation made. For the nearest neighbours we have,

$$2\phi_1 = -\{Q(u^2+v^2+w^2) + 2R(uv+vw+wu)\}$$
$$2\phi_2 = -\{Q(u^2+v^2+w^2) + 2R(-uv+vw-wu)\}$$
$$2\phi_3 = -\{Q(u^2+v^2+w^2) + 2R(-uv-vw+wu)\}$$
$$2\phi_4 = -\{Q(u^2+v^2+w^2) + 2R(uv-vw-wu)\}$$

For the second neighbours we have,

$$2\phi_5 = -\{Su^2 + U(v^2+w^2) + 2W(vw)\}$$
$$2\phi_9 = -\{Sv^2 + U(u^2+w^2) + 2W(wu)\}$$
$$2\phi_{13} = -\{Sw^2 + U(u^2+v^2) + 2W(uv)\}$$
$$2\phi_6 = -\{Su^2 + U(v^2+w^2) + 2W(vw)\}$$
$$2\phi_{11} = -\{Sv^2 + U(u^2+w^2) + 2W(uw)\}$$
$$2\phi_{16} = -\{Sw^2 + U(u^2+v^2) + 2W(uv)\}$$
$$2\phi_7 = -\{Su^2 + U(v^2+w^2) - 2W(vw)\}$$
$$2\phi_{12} = -\{Sv^2 + U(u^2+w^2) - 2W(uw)\}$$
$$2\phi_{15} = -\{Sw^2 + U(u^2+v^2) - 2W(uv)\}$$
$$2\phi_8 = -\{Su^2 + U(v^2+w^2) - 2W(vw)\}$$
$$2\phi_{10} = -\{Sv^2 + U(u^2+w^2) - 2W(uw)\}$$
$$2\phi_{14} = -\{Sw^2 + U(u^2+v^2) - 2W(uv)\}$$

For the third neighbours we have

$$2\phi_{17} = \delta u^2 + \alpha(v^2+w^2) + uv(2\beta) + vw(2\gamma) + wu(2\beta)$$
$$2\phi_{18} = \delta v^2 + \alpha(u^2+w^2) + uv(2\beta) + vw(2\beta) + wu(2\gamma)$$
$$2\phi_{19} = \delta w^2 + \alpha(u^2+v^2) + uv(2\gamma) + vw(2\beta) + wu(2\beta)$$
$$2\phi_{20} = \delta u^2 + \alpha(v^2+w^2) - uv(2\beta) + vw(2\gamma) - wu(2\beta)$$
$$2\phi_{24} = \delta v^2 + \alpha(u^2+w^2) - uv(2\beta) - vw(2\beta) + wu(2\gamma)$$
$$2\phi_{28} = \delta w^2 + \alpha(u^2+v^2) + uv(2\gamma) - vw(2\beta) - wu(2\beta)$$
$$2\phi_{26} = \delta u^2 + \alpha(v^2+w^2) + uv(2\beta) - vw(2\gamma) - wu(2\beta)$$
$$2\phi_{21} = \delta v^2 + \alpha(u^2+w^2) - uv(2\beta) + vw(2\beta) - wu(2\gamma)$$
$$2\phi_{25} = \delta w^2 + \alpha(u^2+v^2) - uv(2\gamma) - vw(2\beta) + wu(2\beta)$$
$$2\phi_{23} = \delta u^2 + \alpha(v^2+w^2) - uv(2\beta) - vw(2\gamma) + wu(2\beta)$$
$$2\phi_{27} = \delta v^2 + \alpha(u^2+w^2) + uv(2\beta) - vw(2\beta) - wu(2\gamma)$$
$$2\phi_{22} = \delta w^2 + \alpha(u^2+v^2) - uv(2\gamma) + vw(2\beta) - wu(2\beta)$$

6. Expressions for the Elastic Constants

If we consider the unit cube in the case of diamond lattice, it is found that there are four similar pairs of points of each kind. Hence the total deformation energy is four times the summation over all the different types of pairs of points. The force constant P does not enter the discussion here since only the change in the mutual energy of pairs of points is considered. Carrying out the summation over all pairs and dividing by the volume of the unit cube, the energy density W is found to be given by

$$\begin{aligned} W = {} & (e_{xx}^2 + e_{yy}^2 + e_{zz}^2)\left\{ -\frac{1}{d}(Q + 8U + 9\delta + 2\alpha)\right\} \\ & + (e_{xx}e_{yy} + e_{yy}e_{zz} + e_{zz}e_{xx})\left\{ -\frac{1}{d}(R + 4W - 6\beta + \gamma)\right\} \\ & + (e_{xy}^2 + e_{yz}^2 + e_{zx}^2)\left\{ -\frac{1}{2d}[Q + R + 4(U + S + W) \right. \\ & \qquad \left. + \delta + 10\alpha - 6\beta + \gamma]\right\} \\ & + (e_{xy}^2 + e_{yz}^2 + e_{zx}^2)\left\{\frac{1}{d}\frac{(R + 2\beta - 3\gamma)^2}{Q + 3\Sigma}\right\} \end{aligned}$$

here $e_{xx} = \dfrac{\partial u}{\partial x}$ and $e_{xy} = \dfrac{\partial u}{\partial y} + \dfrac{\partial v}{\partial x}$.

The strain energy W in terms of the elastic constants is given by

$$\begin{aligned} W = {} & \tfrac{1}{2} C_{11}(e_{xx}^2 + e_{yy}^2 + e_{zz}^2) + C_{12}(e_{xx}e_{yy} + e_{yy}e_{zz} + e_{zz}e_{xx}) \\ & + \tfrac{1}{2} C_{44}(e_{xy}^2 + e_{yz}^2 + e_{zx}^2) \end{aligned}$$

Identifying the two expressions for W

$$C_{11} = -\left\{\frac{Q + 8U + 9\delta + 2\alpha}{d}\right\}$$

$$C_{12} = -\left\{\frac{R + 4W - 6\beta + \gamma}{d}\right\}$$

$$C_{44} = -\left\{\frac{Q + R + 4(U + S + W) + \delta + 10\alpha - 6\beta + \gamma}{2d}\right\} + \frac{(R + 2\beta - 3\gamma)^2}{(Q + 3\Sigma)} \times \frac{1}{d}.$$

We may remark that the effect of the third neighbours is of the same order of magnitude as that of the second neighbours. Ramanathan has obtained the following values for the constants.

$$Q = -1{\cdot}39 \times 10^5; \quad R = -0{\cdot}858 \times 10^5; \quad S = -0{\cdot}005 \times 10^5$$

$$U = -0{\cdot}131 \times 10^5; \quad W = -0{\cdot}114 \times 10^5; \quad \Sigma = -0{\cdot}06 \times 10^5$$

and $\Omega = 0{\cdot}005 \times 10^5$ dynes per cm. where $3\Sigma = 2\alpha + \delta$ and $3\Omega = \beta + \epsilon + \gamma$.

7. Numerical Evaluation

In the expressions for C_{11}, C_{12} and C_{44} the constants α, β, γ, δ, ϵ appear separately. But Ramanathan has evaluated only the constants $(2\alpha + \delta)$ and $(\beta + \epsilon + \gamma)$. Hence there arises a slight difficulty in the numerical computation of the values of the elastic constants. α and δ are the force constants for the two atoms that are at the same distance from the origin and whose x co-ordinates are in the ratio 1 : 3. With the help of a model of diamond, it can be seen from the position of the two atoms and the nature of the displacement that α and δ would be of the same sign and that α would be definitely less than δ. As regards the magnitude of α, we may surmise that it would be somewhere between $\frac{1}{2}\delta$ and $\frac{1}{3}\delta$.

Table I

Elastic constants	$\alpha = \delta$, $\beta = -2\gamma$	$2\alpha = \delta$, $\beta = -2\gamma$	$3\alpha = \delta$, $\beta = -2\gamma$
$C_{11} \times 10^{-12}$ ..	8·7	9·38	9·77
$C_{12} \times 10^{-12}$ ..	3·88	3·88	3·88
$C_{44} \times 10^{-12}$ ..	4·37	4·20	4·11

It will be seen from Table I that changes in α produce considerable changes in the values of the elastic constants deduced from the formulæ.

The constants β and γ represent forces acting in a perpendicular direction to that of the displacement and they are, in consequence, of small magnitude. Considerations similar to those stated in respect of α and δ indicate that γ and β are of opposite sign and that $|\gamma| < |\beta|$. We assume $\beta = -2\gamma$ as a near enough approximation.

The most probable values of the elastic constants of diamond deduced from the present investigation, may be given as

$$C_{11} = 9{\cdot}6 \times 10^{12}; \quad C_{12} = 3{\cdot}9 \times 10^{12}; \quad C_{14} = 4{\cdot}2 \times 10^{12} \text{ dynes/cm}^2.$$

These values show satisfactory agreement with the values experimentally determined by the ultrasonic method by Bhagavantam and Bhimasenachar (1946) who get the following values.

$$C_{11} = 9{\cdot}5 \times 10^{12}; \quad C_{12} = 3{\cdot}9 \times 10^{12}; \quad C_{44} = 4{\cdot}3 \times 10^{12} \text{ dynes/cm.}^2$$

The bulk modulus of diamond $K = \frac{1}{3}(C_{11} + 2C_{12})$ comes out as $5{\cdot}8 \times 10^{12}$ if the theoretical values are substituted. This result agrees with the value obtained by Williamson who gets $5{\cdot}6 \times 10^{12}$. Adams obtained a value $6{\cdot}3 \times 10^{12}$ for K and this is rather high.

In conclusion, the author wishes to express his sincere thanks to Prof. Sir C. V. Raman, F.R.S., N.L., for suggesting this problem and for the many illuminating discussions he had with him. He also thanks Dr. G. N. Ramachandran for his kind interest in this work.

8. Summary

Expressions for the elastic constants of diamond have been derived in terms of the force constants calculated by Ramanathan which express the interaction of any atom with its 28 neighbours. The calculated values are: $C_{11} = 9{\cdot}6 \times 10^{12}$; $C_{12} = 3{\cdot}9 \times 10^{12}$; $C_{44} = 4{\cdot}2 \times 10^{12}$ dynes/cm.^{2} while the values experimentally determined by Bhagavantam and Bhimasenachar are:

$$C_{11} = 9{\cdot}5 \times 10^{12};\quad C_{12} = 3{\cdot}9 \times 10^{12};\quad C_{44} = 4{\cdot}3 \times 10^{12} \text{ dynes/cm.}^2$$

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SYNERESIS OF SODIUM OLEATE GELS IN ORGANIC SOLVENTS

Part III. Effect of Temperature on the Syneresis of Sodium Oleate Gels in Pinene

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Changes in temperature affect the syneresis of different gels in different manner. In gels of silicic acid, an increase in temperature increases the syneresis. Ferguson and Applebey[1] have observed that the velocity of syneresis of silicic acid gels is approximately doubled for each 10° rise in temperature. Similarly Bonnell[2] has concluded that increased temperature accelerates the syneresis of silicic acid gels and causes it to proceed to a further stage. Prakash and Dhar[3] have also found that not only the syneresis of some inorganic jellies is higher at higher temperatures but also the temperature coefficient of their syneresis at higher temperatures is larger than that at lower temperatures.

The increase in temperatures causes the reverse effect on the syneresis of the geranin gels (*cf.* Lipatov[4]). Prasad and co-workers[5] have observed that the syneresis of sodium oleate gels in pinene also decreases with increasing temperature. In the present investigation the syneresis of sodium oleate gels in pinene has been studied thoroughly and systematically over a long range of temperature.

Experimental

1. *Maintenance of temperature.*—An air thermostat was used for maintaining the temperature at 30°, 40° and 50° C. The temperature inside the thermostat was maintained within $\pm 0{\cdot}1°$.

For maintaining the temperatures at 0°, 15° and 25° C., a thermos flask was used. To maintain 0° C., the test-tubes containing the gels were placed vertically in powdered ice kept in the flask. At frequent intervals water formed in the flask was removed and fresh ice was added. To maintain 15° C., ice was added to water to cool it to the required temperature. The test-tubes were clamped vertically such that the level of the gel in the test-tube was lower than that of water in the flask. Occasionally, a little water was removed from the flask and a small piece of ice was added. The temperature was maintained with an accuracy of $\pm 0{\cdot}4°$ C. A similar procedure was followed for obtaining the temperature of 25° C.

2. *Preparation of the gels.*—The gels were prepared in test-tubes of internal diameter 1·70 cm., by dissolving the requisite quantity of sodium oleate (0·10 g., 0·15 g., 0·20 g.) in 10 c.c. of pinene by the procedure adopted in Part I.[6] The gels were allowed to set in either the thermostat or the thermos flask depending on the temperature at which the syneresis was studied. The amount of syneresis was measured by the method of Prasad and co-workers.[5]

Results

The results obtained are given in the following tables in which Y and t carry the same meaning as in Parts I and II and Q represents the amount in grams of sodium oleate in 10 c.c. of the solvent.

Table I

Q = 0·10

t in hours	Y at various temperatures					
	0°	15°	25°	30°	40°	50°
1	11·58	10·88	8·04	7·03	5·38	3·53
2	14·48	12·54	10·92	9·32	7·26	5·28
3	15·68	15·51	11·60	10·87	10·07	6·49
5	16·81	15·84	13·85	12·77	11·03	8·75
7	17·34	16·28	15·15	13·67	12·84	10·41

Table II

Q = 0·15

t in hours	Y at various temperatures			
	0°	30°	40°	50°
1	9·36	4·72	3·63	2·48
2	12·27	6·84	5·60	3·83
3	13·85	8·05	6·67	4·75
5	14·36	11·10	8·85	6·13
7	15·48	12·89	10·41	8·30

TABLE III

Q = 0·20

t in hours	Y at various temperatures			
	0°	30°	40°	50°
1	7·12	3·46	2·58	1·76
2	9·08	4·92	4·37	2·92
3	10·39	6·28	5·40	3·78
5	12·12	8·08	7·25	4·98
7	12·64	10·43	8·75	6·43

DISCUSSION OF RESULTS

It will be seen from the above tables that for all the three concentrations of the gel studied the amount of liquid exuded is greatest at the lowest temperature, and decreases as the temperature is increased. This observation is similar to that of Prasad and co-workers. The Y–*t* curves in all cases are smooth rising (*cf.* Part II[7]) and their initial rise falls off gradually as the temperature is increased.

At any temperature the values of the unimolecular constant (Km) decrease as the time interval is increased (*cf.* Part II[7]), and at any given interval of the time they increase as the temperature is decreased.

The validity of the relation $Y^n = kt$ for different temperatures was examined by plotting the values of log Y against those of log *t* for gels containing 0·1 g. of the soap. It will be seen that the graphs (Fig. 1) for syneresis at 25° C. and above are straight lines, thereby indicating that the relation is followed for these temperatures. However, the graphs for syneresis at 0° C. and 15° C. are pairs of intersecting straight lines; the change in the direction of the initial line taking place after the syneresis has reached about 16%. This establishes that there are two stages involved in the exudation of the syneretic liquid, the earlier one being more rapid than the latter. The second stage could not be observed at temperatures besides 0° C. and 15° C. because the maximum time interval studied is not sufficient for the syneresis to reach this stage. This view was confirmed when the gels were allowed to synerise for longer period at 30° C. (*cf.* Part II[7]).

There does not seem to be any direct relationship between the amount of syneresis and temperature at which a gel synerises. However, an interest-

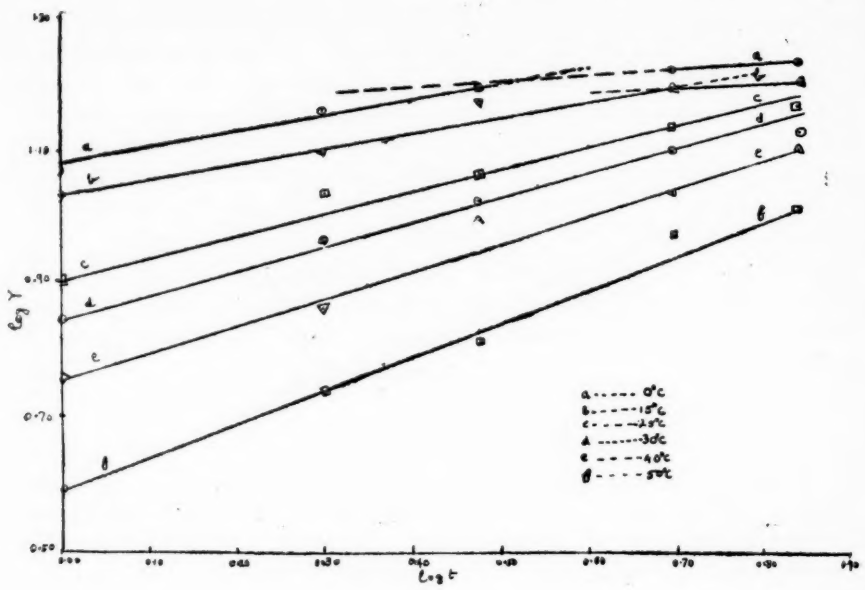

FIG.

ing observation is made when the values of Y at each time interval are plotted against temperature in the case of 1% gel. The points for each time interval lie on a curve and all the curves appear to converge and meet the temperature axis at one point (*cf.* Fig. 2). This shows that at this temperature,

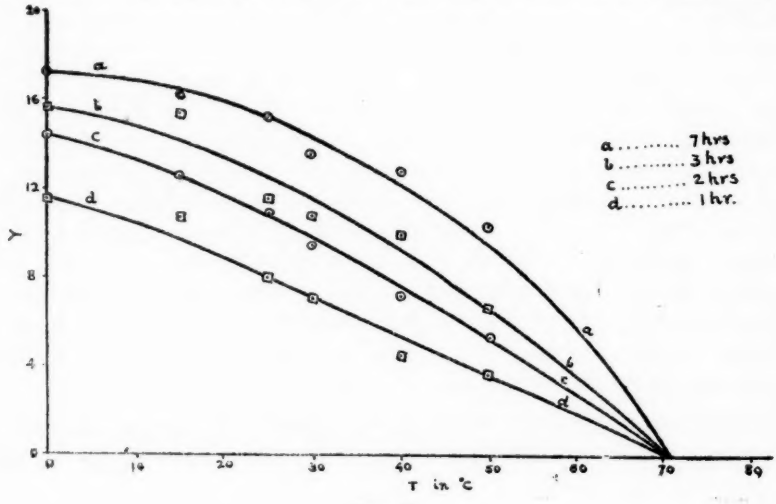

FIG. 2

namely 71° C., no syneresis takes place whatever be the time interval for which the gel is maintained at this temperature. This conclusion has been experimentally verified. Curiously enough it has been found experimentally that the gelation temperature, that is, the temperature at which the gel-forming solution of this concentration just sets to a gel, is 70° C. It may therefore be generalised that if a gel is maintained at its gelation temperature, no syneresis would at all take place, that is, the gel would be most stable.

The above discussion shows that two important observations have been made in this investigation, namely, (i) the gels of sodium oleate in pinene do not synerise at their gelation temperatures and (ii) the amount of synereticum exuded in a given interval of time since the commencement of syneresis increases with a decrease in the temperature, at which the syneresis is studied.

It is known that the gels of the soaps of various metals in organic solvents are prepared in an identical manner, namely, by dissolving a certain amount of the soap in the solvent at a high temperature, near about the boiling point of the solvent, and then cooling the resulting solution. Hence, it will not be far from truth if it is assumed that the mechanism of formation of all these gels and probably their structure are more or less the same. However, only some of these gels, such as gels of sodium oleate in pinene or xylene, exhibit the phenomenon of syneresis, while others, such as gels of sodium oleate in Nujol or of sodium stearate in pinene, are non-syneretic. This indicates that syneresis is a special property of some gels and is not dependent on the mechanism of gel-formation or the gel structure. The special characteristic of a syneretic gel is the instability of its structure formed when the gel sets; this condition would be determined essentially by the nature of the gel-forming substance and the dispersion medium, but it may be effected by the rate of cooling of the solution of the gel-forming substances in the dispersion medium, and its concentration.

Sodium oleate and pinene give rise to an unstable system. It is observed that this system remains quite stable when a solution of sodium oleate in pinene made at 140° C. is cooled to the gelation temperature, that is, the temperature at which the system sets to a gel. It is probable that certain optimum conditions prevail at this temperature which maintain the system in an equilibrium state, that is, the system remains unaltered so long as the temperature is maintained at the gelation temperature of the system, and hence no syneresis is observed at the gelation temperature.

If these gels are allowed to cool below the gelation temperature, the changes in equilibrium conditions caused by the lowering of the temperature

are in the direction of reduced stability. Hence the structure formed at the gelation temperature becomes unstable and syneresis results on account of the displacement of the system to attain stability at that temperature. The lower the temperature to which the gel is cooled, the greater is the deviation from the equilibrium conditions prevailing at the gelation temperature. Hence at lower temperatures the unstability of gel structure formed at the gelation temperature is greater causing a larger amount of syneresis.

It is observed in the previous paper[6] that the exudation of liquid is rapid in the early stages of syneresis but subsequently it slows down. On keeping these gels for a very long time (several months) it is found that ultimately almost all the liquid is exuded and only a small flake of the solvated soap settles down at the bottom. This shows that once the syneresis commences, the equilibrium point is very remote, that is, the equilibrium is attained only after a long lapse of time, indicating that not only the structure of the fibrils which go to form the soap gels is broken but even the structure of the entities which go to form the fibrils at the lower temperature is more or less completely smashed.

Summary

The syneresis of sodium oleate gels in pinene has been found to increase with a decrease in the temperature at which they are allowed to synerise. There does not seem to be any direct relation between syneresis and temperature. When the graphs of syneresis against temperature for each interval of time are extrapolated, all the graphs meet the temperature axis at a single point which agrees closely with the gelation temperature of the gel; this leads to the inference that no syneresis takes place at the gelation temperature which has been actually verified. An explanation has been advanced for the observed results.

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SYNERESIS OF SODIUM OLEATE GELS IN ORGANIC SOLVENTS

Part IV. Effect of Concentration on the Syneresis of Sodium Oleate Gels in Pinene and Xylene

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Holmes, Kaufmann and Nicholas[1] were the first to observe that syneresis in silica gels increases with an increase in the concentration of silicic acid. This fact has been confirmed by Ferguson and Applebey[2] and by Bonnell[3]; however, Bonnell has also shown that for very dilute gels (concentration less than 4%) syneresis increases with decrease in concentration.

Lipatov and Korobova[4] have found that the velocity of syneresis of geranin gels increases as the concentration of the gel is increased. Mukoyama[5] has also observed that, at constant alkali content, syneresis of gels of cellulose acetate increases with increase in the concentration. However, Atsuki and Sobue[6] state that more dilute the viscose gel is, the greater is the syneresis.

Prasad, Hattiangdi and Mathur[7] studied the kinetics of syneresis of sodium oleate gels in pinene of concentrations varying from 0·5% to 1·25% and have observed that an increase in the concentration of the soap in the gel decreases the syneresis. In the present investigation an attempt has been made to extend the work of Prasad and co-workers in order to see whether these gels show any effect similar to that observed in the case of silica gels. Also, the effect of concentration on the syneresis of sodium oleate gels in xylene has been investigated for the first time.

Experimental

Gels of sodium oleate in pinene and xylene were prepared in test-tubes of internal diameter of 1·38 cm. by the method described in Part II.[8] All the gels were allowed to set in a thermostat maintained at 30° ± 0·1° C. The amount of syneresis was measured by the method of Prasad and co-workers.[7] The different concentrations studied were 0·05 g., 0·08 g., 0·10 g., 0·15 g., 0·20 g., and 0·25 g. of the soap in 10 c.c. of pinene and 0·05 g., 0·08 g., 0·10 g., 0·15 g. and 0·25 g. of the soap in 10 c.c. of xylene. Higher concentrations of the soap could not be used because at these concentrations the soap dissolves in the two solvents only with very great difficulty and the gels formed are not homogeneous.

Results

The results obtained are given in the following tables in which t and X carry the same meaning as in Part II and Q in Part III.

Table I

Syneresis of sodium oleate gels in pinene

t in hours	X for gels containing					
	Q=0·05	Q=0·08	Q=0·10	Q=0·15	Q=0·20	Q=0·25
1	1·261	1·139	0·975	0·720	0·489	0·313
2	1·470	1·281	1·150	0·964	0·691	0·500
3	1·602	1·426	1·322	1·161	0·900	0·685
5	1·846	1·610	1·538	1·290	1·125	0·932
7	1·971	1·750	1·643	1·507	1·337	1·178
10	2·238	1·972	1·848	1·696	1·620	1·466
∞	4·44	3·75	3·60	2·63	1·92	1·51

Table II

Syneresis of sodium oleate gels in xylene

t in minutes	X for gels containing				
	Q=0·05	Q=0·08	Q=0·10	Q=0·15	Q=0·25
5	1·431	1·330	1·247	1·160	1·025
10	1·720	1·663	1·555	1·459	1·361
15	2·030	1·862	1·780	1·730	1·606
20	2·093	2·017	1·890	1·836	1·821
30	2·417	2·307	2·166	2·107	2·068
∞	3·40	3·28	3·23	3·00	2·63

Discussion of Results

It is seen from the above tables that in the case of sodium oleate gels in pinene and xylene the rate of syneresis and the amount of synereticum exuded out in any given interval of time are greater for the dilute gels than

for the concentrated ones, and they gradually decrease with increase in concentration. The graphs of X against t are smooth rising curves and not S-shaped in all cases (*cf.* Parts II and III[8,9]); those for the gels in pinene are shown in Fig. 1.

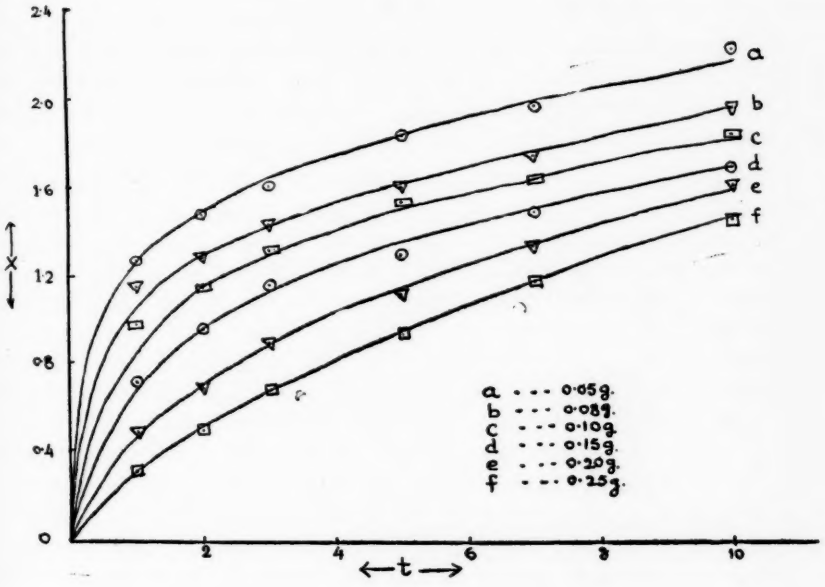

FIG. 1

The relation $X^n = kt$ has been found to hold good for gels of all concentrations in xylene and pinene. The values of n calculated from the graph are given in the last row of Tables I and II. The values of n are not 2 in all cases and decrease as the concentration is increased.

Gapon[10] has expressed the relation between syneresis and concentration by the equation $\frac{X_s}{(P_0 - P)} = H$, where X_s is the amount of syneresis expressed as percentage of the initial quantity of the solvent for the concentration of the solute P, P_0 is the concentration at which no syneresis takes place, and H is the syneresis constant. It follows from this that graphs of X_s against P must be straight lines, as P_0 can be assumed to be constant for a particular gel system. If the same amount of the solvent is taken in each case, then X_s can be replaced by X, the amount of syneresis actually obtained in this investigation and P is the same as Q. To test the validity of this

relation in the case of sodium oleate gels in pinene and xylene, the values of X after the same interval of time were plotted against Q and the graphs obtained were definitely not straight lines. Gapon's equation is, therefore, not applicable to the syneresis of sodium oleate gels in pinene and xylene and hence cannot be taken as a general equation.

The most important result obtained in this investigation is that the gels of lower concentration synerise more than those of higher concentration, that is, syneresis decreases with an increase in the concentration of the gel. This may be due to one or more of the following causes:

(i) It has been stated in the previous paper (*cf.* Part III[9]) that (*a*) gelation of a gel-forming system takes place at its gelation temperature because of certain equilibrium conditions present in the system at that temperature and (*b*) that when a gel is cooled below its gelation temperature, due to the changes in equilibrium conditions caused by the lowering of temperature, the gel structure becomes unstable causing syneresis. It is quite possible that the equilibrium conditions necessary for gel-formation are different at different temperatures. It has been observed experimentally that the gelation temperature increases with increase in concentration that is, a gel-forming system of a higher soap content sets at a higher temperature than one of a lower soap content. Hence, the equilibrium conditions in which a gel of higher concentration has been formed are different from those of the formation of gel of lower concentration and therefore the structure of the entities forming the gel in the two cases will be different. This difference in structure probably results in increasing the ability of gels of higher concentrations to withstand the deviations in equilibrium conditions caused by the lowering of temperature below the gelation temperature. Hence, when cooled to the same temperature, the gels of higher concentration synerise less than those of lower concentrations, although the changes in the equilibrium conditions may be greater in the case of gels of higher concentrations than in those of lower concentrations because of their higher gelation temperatures.

(ii) It is observed during the preparation of these gel-forming systems that an increase in the concentration of soap in the solvent increases the viscosity of the solution to a large extent. Since a viscous system offers a larger resistance to forces of shear and deformation, it appears that the increased viscosity of the more concentrated gel-forming system gives rise to a gel structure which offers greater resistance to changes in equilibrium conditions than gels of lower concentrations, and hence favours a decrease in syneresis with increase in concentration.

(iii) When an aqueous solution of calcium acetate is poured into alcohol, a gel results which rapidly breaks up into crystals. The addition of sodium oleate to this system prevents crystallisation and the gel obtained remains stable. This has been attributed to the fact that sodium oleate inhibits crystallisation of calcium acetate. In the systems of sodium oleate in pinene, it has been observed that below a concentration of 0·4% gels are not formed and crystallisation occurs. Increasing the amount of sodium oleate to about 0·5% results in gel-formation. This may also be due to the same cause as in the case of calcium acetate gels. Hence further increase in the amount of sodium oleate can be expected to increase the stability of the gel thereby decreasing syneresis.

Summary

The effect of concentration on the syneresis of sodium oleate gels in pinene and xylene has been investigated. The initial rate of syneresis and the total amount of synereticum given out in a given interval of time since the commencement of syneresis are larger for gels of lower concentrations and decrease with an increase in the concentration of the gels. An explanation has been advanced for this behaviour.

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SYNERESIS OF SODIUM OLEATE GELS IN ORGANIC SOLVENTS

Part V. Syneresis of Sodium Oleate Gels in Mixtures of Organic Solvents

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Various investigators have pointed out the importance of the nature of the dispersion medium on the syneresis of gels. Usually the dispersion medium has been changed by the addition of other substances, such as acids, alcohols and others. Very few investigators have studied the syneresis of the same gel-forming substance in different media. Hardy[1] observed that the syneresis of azomethine gels starts in a few minutes in an ether gel, in a few hours in an alcohol or an aldehyde gel and in a few days in a carbon tetrachloride gel. Le Blanc and Kroger[2] have noticed that the syneresis of caoutchouc gels in benzene starts earlier than in carbon tetrachloride; the velocity of the main amount exuded in both the solvents is the same but the final amount exuded by the gel in carbon tetrachloride is somewhat greater.

It has been observed in a previous communication[3] that gels of sodium oleate in xylene synerise more rapidly than those in pinene. In the present investigation, an attempt has been made to study the syneresis of sodium oleate gels in mixtures of (*a*) xylene and toluene and (*b*) xylene and pinene.

Experimental

(*a*) 0·100 g. of sodium oleate was weighed out into five different test-tubes of the same internal diameter (1·65 cm.) which were filled with several mixtures of xylene (A) and toluene (B). It was observed that if the mixtures contained more than 70% by volume of toluene, the soap does not dissolve completely and the gels obtained are not homogeneous. Hence mixtures containing more than 70% toluene were not used.

(*b*) 0·100 g. of sodium oleate was weighed out into seven different test-tubes of the same internal diameter (1·65 cm.) which were filled with several mixtures of xylene (A) and pinene (C).

The test-tubes were placed in an oil-bath, the temperature of which was maintained at 120°–25° C. in the case of mixtures of xylene and toluene and at 130°–35° C. in the case of mixtures of xylene and pinene, and the

contents of the test-tubes stirred till all the soap had dissolved. Then a long condensing tube was attached to each test-tube and the test-tubes were allowed to stand in the bath till all the bubbles had disappeared. The test-tubes were then tightly corked and transferred to a thermostat or a thermos flask depending on the temperature at which readings were taken. At definite intervals of time (t) after the gels had set, the amount of synereticum (X) in each test-tube was measured by the method followed in Part II.[3] The temperatures used were 30° C. and 40° C. in the thermostat and 20° C. in the thermos flask.

Sodium oleate used was of the B.D.H. quality and the xylene used was obtained from S. B. Penick & Co., New York. Toluene was obtained from May & Baker, Ltd., and pinene from the City Chemical Corporation, New York.

The results obtained are given in Tables I and II.

Discussion of Results

It is seen from Table I that in the case of gels in mixtures of xylene and toluene the syneresis increases with an increase in the amount of toluene in the mixture. This fact is seen at all the temperatures. Also, the amount of syneresis at any one composition of the mixture is greatest at 20° C. and decreases as the temperature is increased. The effect of temperature on gels in mixtures of solvents is therefore similar to that on gels in these pure solvents (*cf.* Part III of this series[4]). The graphs of syneresis against composition of the mixture are more or less straight lines for all the time intervals

Table I

Values of X for gels in mixtures of xylene and toluene at various intervals

Composition of the mixture		Temperature 20° C.				Temperature 30° C.				Temperature 40 C.			
A	B	15 min.	30 min.	1 hr.	2 hr.	15 min.	30 min.	1 hr.	2 hrs.	15 min.	30 min.	1 hr.	2 hrs.
10 c.c.	0 c.c.	1·850	2·111	2·300	2·416	1·731	1·913	2·054	2·168	1·658	1·784	1·911	2·020
8 c.c.	2 c.c.	1·960	2·232	2·415	2·550	1·827	2·054	2·146	2·290	1·760	1·915	2·075	2·079
6 c.c.	4 c.c.	2·091	2·346	2·553	2·683	1·950	2·184	2·309	2·440	1·894	2·019	2·105	2·174
4 c.c.	6 c.c.	2·207	2·473	2·674	2·805	2·040	2·288	2·411	2·499	1·993	2·139	2·231	2·277
3 c.c.	7 c.c.	2·267	2·555	2·759	2·863	2·100	2·358	2·492	2·600	2·030	2·235	2·320	2·377

TABLE II

Values of X for gels in mixtures of xylene and pinene at various intervals

Composition of the mixture		Temperature 20° C.				Temperature 30° C.				Temperature 40° C.			
A	C	15 min.	30 min.	1 hr.	2 hrs.	15 min.	30 min.	1 hr.	2 hrs.	15 min.	30 min.	1 hr.	2 hrs.
10 c.c.	0 c.c	1·850	2·111	2·300	2·416	1·731	1·913	2·054	2·168	1·658	1·784	1·911	2·020
9 c.c.	1 c.c.	1·962	2·344	2·464	2·600	1·906	2·118	2·352	2·462	1·814	2·111	2·168	2·250
8 c.c.	2 c.c.	2·022	2·390	2·592	2·652	1·886	2·220	2·485	2·545	1·708	2·126	2·340	2·422
6 c.c.	4 c.c.	1·643	1·979	2·475	2·595	1·471	1·887	2·350	2·513	1·147	1·700	2·104	2·330
4 c.c.	6 c.c.	1·094	1·604	1·944	2·196	1·136	1·326	1·800	2·087	0·640	1·057	1·384	1·867
2 c.c.	8 c.c.	0·894	1·148	1·464	1·742	0·723	0·922	1·338	1·607	0·217	0·520	0·907	1·266
0 c.c.	10 c.c.	0·650	0·858	1·187	1·398	0·460	0·668	1·048	1·189	0·166	0·324	0·635	0·967

studied, indicating the possibility of an additivity law. The graphs of syneresis against composition at 20° C. are shown in Fig. 1. Since no gels are formed in pure toluene with 0·10 g. of the soap, the validity of the additivity law cannot be tested in any case.

It is seen from Table II that on increasing the percentage of pinene in the mixture of xylene and pinene, the amount of syneresis of gels at first increases, reaches a maximum in a mixture containing 80% xylene and 20% pinene, and then gradually falls off. The graphs of syneresis against composition of the mixture are S-shaped for all the time intervals and temperatures studied; those in the case of syneresis at 20° C. are shown in Fig. 2. The amount of synereticum given out by a gel in pure xylene is greater than that given out by the same gel in pure pinene. Hence, it would be expected that on increasing the amount of pinene in the mixture the amount of synereticum should continually decrease.

Palit and co-workers[5] have shown that in the case of organic mixtures containing a glycol as one component, the solubility of soap reaches a maximum value at intermediate compositions of the mixture. Probably in the mixtures of pinene and xylene the solubility has an optimum value in the mixture containing 80% xylene and 20% pinene. Since the same amount of soap is used in all the mixtures the amount of supersaturation will be least in the mixture of 80% xylene and 20% pinene and hence the gel formed will be weaker (*cf.* Part IV[6]). Therefore the syneresis of the gel in the

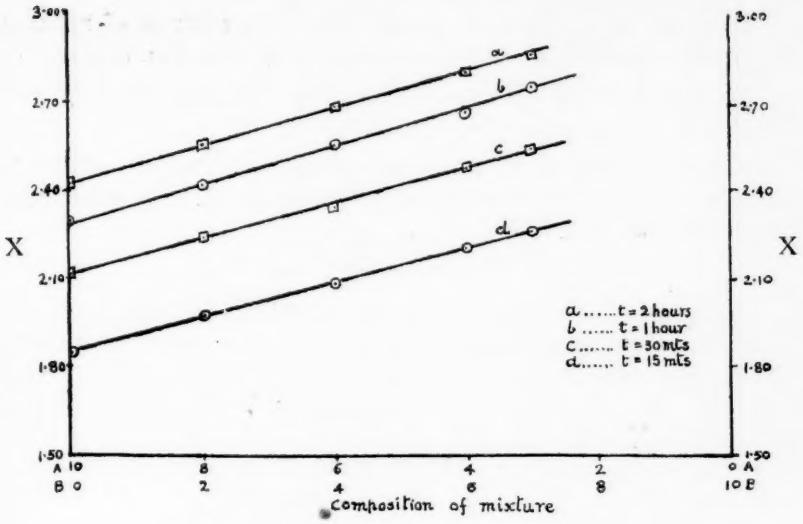

FIG. 1

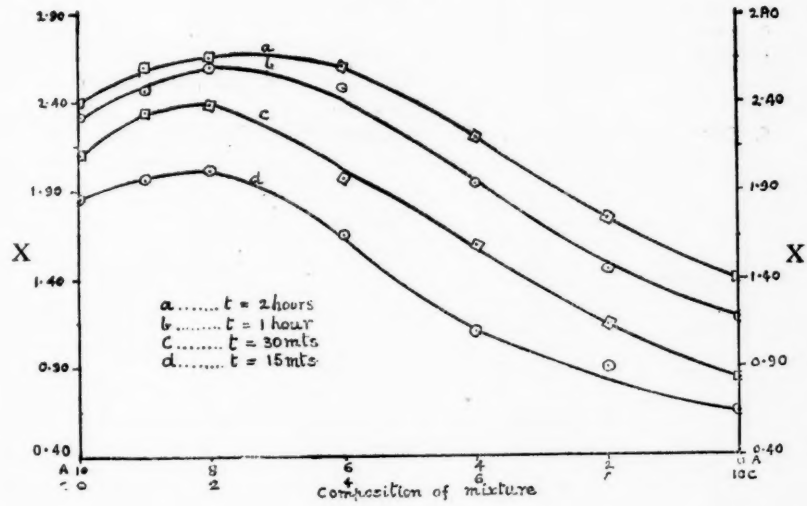

FIG. 2

mixture of 80% xylene and 20% pinene would be maximum. Such an effect is not observed in the mixtures of toluene and xylene, probably because both these solvents belong to the same homologous series and the solubility in these solvents probably follows the additivity law,

It is also observed, as in the case of gels in mixtures of xylene and toluene, that syneresis at a lower temperature is greater than at higher ones.

Further work for the examination of the behaviour of soap gels in mixtures of organic liquids is in progress.

One of the authors (V. S.) is grateful to the authorities of the University of Bombay for the award of a Research Studentship which enabled him to carry out this investigation.

Summary

The rates of syneresis in mixtures of (1) xylene and toluene and (2) xylene and pinene have been investigated. In the case of xylene-toluene mixtures, syneresis seems to be additive whereas in the case of xylene-pinene mixtures, syneresis shows a maximum value in a mixture of 80% xylene and 20% pinene.

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DIFFUSION OF IONS THROUGH SOME INDIAN TIMBERS

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Diffusion processes play an important part in various timber industries, *e.g.*, the treatment of veneers with resins or resin forming systems, preservatives like boric acid, etc. For efficient treatment it is essential that the fundamental laws governing the movement of ions, molecules, etc., through wood are established. A knowledge of these factors is also of interest to the wood seasoning, textile, leather, and paper technologists and the plant physiologist.

Cady and Williams (1935) studied the diffusion of urea, glycerol and lactose into several species of water-saturated soft woods relative to their diffusion in water. More recently the diffusion of salts through green timber has been extensively studied by Christensen in Australia.

Theoretical

Fick's law of diffusion can be mathematically expressed as follows:—

$$q = k\frac{dc}{dx}, \qquad (1)$$

where q is the quantity of the substance flowing through in gm./cm.^{2} sec. at the steady state, k the diffusion constant and $\frac{dc}{dx}$ the concentration gradient. k has the dimensions cm.^{2}/sec. This applies to capillary systems. In the case of space energy systems (pores of molecular dimensions) the concentration at the two surfaces of the membrane are not the same as that in the reservoir and a relation between reservoir and surface concentrations depending on a Henry distribution exists and $\frac{dc}{dx} = T\frac{dc'}{dx}$ where T is the distribution coefficient.

Apparatus

The apparatus employed is shown in Fig. 1. In essentials it consists of 2 chambers made from perspex sheeting with flanges between which the specimen under investigation is fixed, rubber washers being used between the

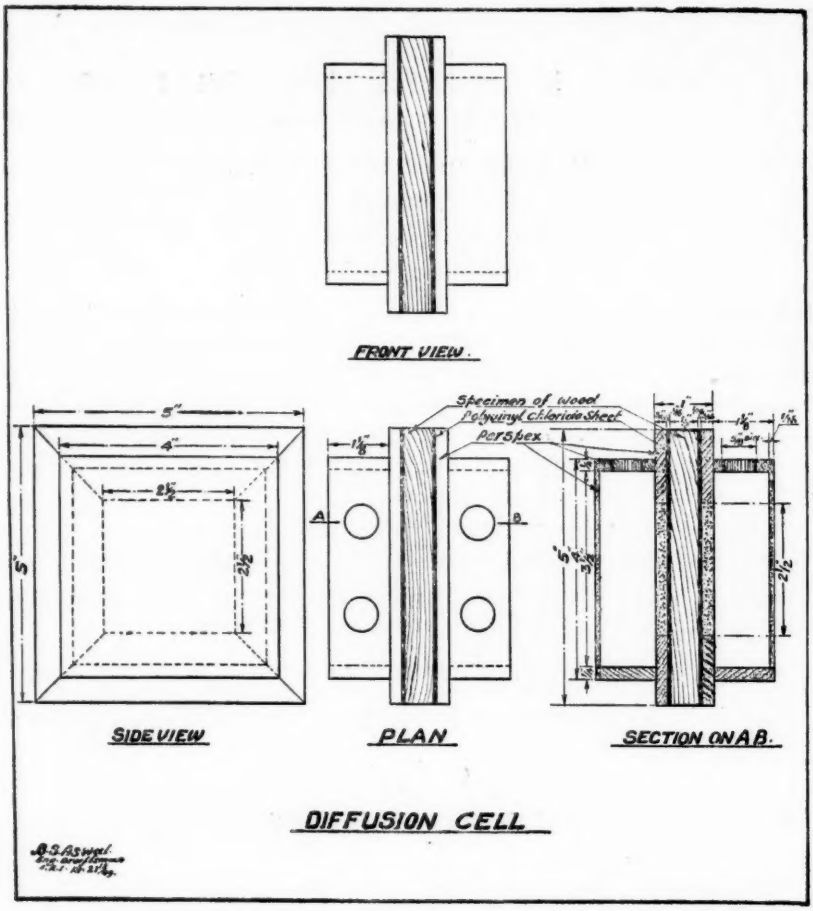

FIG. 1

flanges and the specimen. The tops of the two halves of the diffusion cells were provided with two holes for receiving or emptying the solution or water used in the cells. These were stoppered with a fine capillary to avoid evaporation during the test.

The specimen was placed between the flanges of the cell and the whole assembly was held in a wooden frame fitted with nuts and bolts. Rubber packing between the cell walls and wooden frame helped to prevent damage to the cells.

Materials and Preparation of the Specimens

Canarium strictum (dhup) and *Cullenia excelsa* (karani) were used for most of the experiments.

Specimens were prepared from different locations in 8″ thick discs of the timbers.

They were cut and planed to the size required and were kept under water till wanted for use. Before fitting in the cells, the outer half inch of the edges of the specimens were given three coats of shellac varnish to prevent end leakage. They were further given a coat of paraffin and in other cases thin aluminium foil was used.

In addition to wood, cellophane was also studied.

Procedure of Carrying Out the Tests

After installation of the test specimen in the diffusion cell both compartments of the cell were first filled with distilled water and kept in an air thermostat for a day; the next day the cells were emptied and then one side was filled with distilled water and the other side with the solution of the salt. It is necessary, especially with axial specimens, to pour both the solution and water at the same time and at the same rate, otherwise there is a danger of flow from one side to the other. The holes in the top were then lightly corked and the cells kept in the air thermostat.

At intervals of 24 hours the cells were emptied (again care being taken to empty both sides simultaneously and at the same rate) and analysed according to standard practice. This was continued till the steady state was reached.

From the analytical and other data the diffusion coefficient was calculated according to equation (1).

Results and Discussion

The results of all the experiments are given in Tables I–III and Figs. 2 and 3.

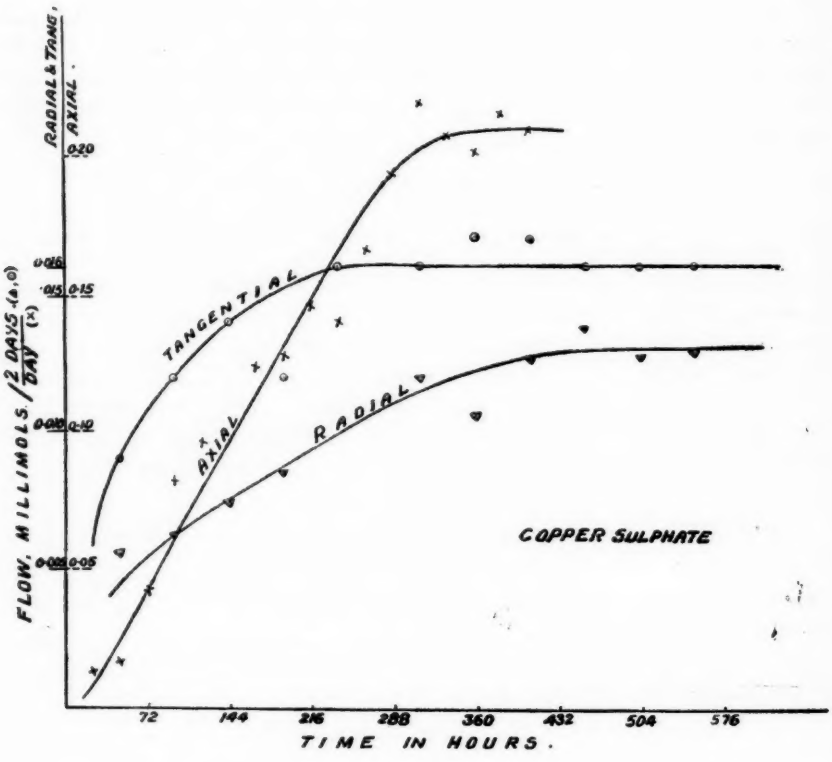

Fig. 2

Time taken to reach steady state.

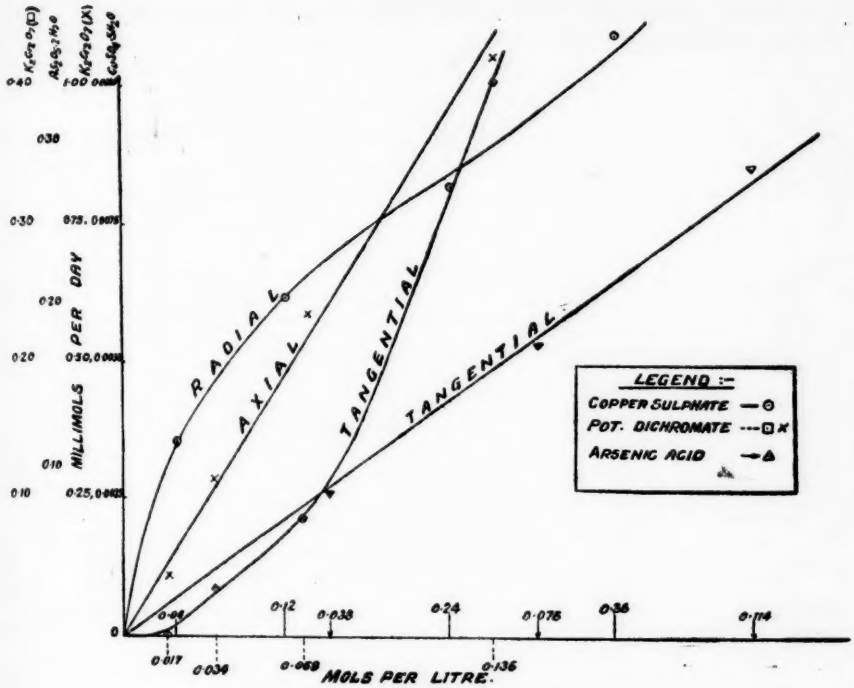

FIG. 3.

Y — Axis - Quantity diffusing through per day at the steady state.
X - Axis - Concentration difference across the membrane.

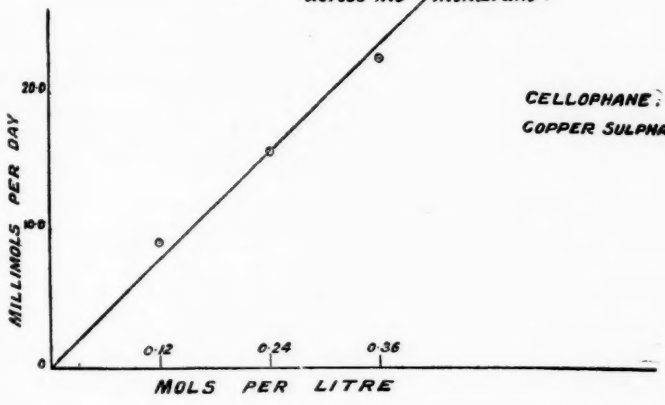

Table I illustrates the influence of increasing concentration gradient on the diffusion constant.

TABLE I

Species and direction of flow	Concentration difference mols./litre	K cm.²/day
1	2	3
	Sodium chloride	
1 *Canarium strictum* Axial II (10)	0·2, 0·4, 1·0, 2·0, 4·0	0·229, 0·380, 0·349, 0·320, 0·267 Mean = 0·309
do I (10)	do	0·233, 0·350, 0·349, 0·326, 0·281 Mean = 0·308
2 *Boswellia serrata* Radial	1·0	0·00136
	Copper sulphate	
3 *Canarium* sp. Axial I (11)	0·04, 0·12, 0·24, 0·36	0·474, 1·235, 0·523, 1·105 Mean = 0·834
4 *Canarium* sp. Axial II (10)	do	*Nil, 0·039, 0·031, 0·112 Mean = 0·061
5 *Canarium* sp. Axial III Unleached (9)	do	0·0398, 0·0607, 0·0663, 0·134 Mean = 0·0752
6 *Canarium* sp. Radial I (3)	do	*Nil, 0·00019, 0·00013, 0·00011 Mean = 0·00014
7 Do II (4)	do	*Nil, 0·00023, 0·00015, 0·00019 Mean = 0·00019
8 *Canarium* sp. Radial III (7) unleached	do	0·00039, 0·00023, 0·00015, 0·00014 Mean = 0·00023
9 *Canarium strictum* Tangential I (12)	do	*Nil, 0·00014, 0·00012, 0·00013 Mean = 0·00013
do II (15)	do	*Nil, 0·00016, 0·00017, 0·00016 Mean = 0·00016
	Potassium dichromate	
10 *Canarium strictum* Axial I (10)	0·017, 0·034, 0·068, 0·136	0·0094, 0·036, 0·059, 0·034 Mean = 0·0346
do II (11)	do	0·261, 0·299, 0·344, 0·309 Mean = 0·303
11 *Cullenia excelsa* Radial I (7)	do	0·0152, 0·0196, 0·0175, 0·0168 Mean = 0·0173
do II (2)	do	0·00156, 0·00525, 0·00759, 0·00525 Mean = 0·00491
12 *Cullenia excelsa* Tangential I (3)	do	0·00048, 0·00668, 0·00798, 0·0188 Mean = 0·00849
do II (8)	do	0·00013, 0·0024, 0·0025, 0·0036 Mean = 0·00216
	Arsenic acid	
13 *Canarium strictum* Axial I (11)	0·038, 0·076, 0·114	0·409, 0·425, 0·414 Mean = 0·416
do II (9)	do	0·205, 0·208, 0·218 Mean = 0·210
14 *Cullenia excelsa* Radial I (6)	do	0·059, 0·0645, 0·070 Mean = 0·0645
do II (7)	do	0·0658, 0·0663, 0·0709, Mean = 0·0677
15 *Cullenia excelsa* Tangential I (5)	do	0·0255, 0·0249, 0·0245 Mean = 0·025
do II (4)	do	0·0161, 0·0148, 0·0157 Mean = 0·0155

* The nil values hove not been considered for the mean.

The agreement between duplicates is satisfactory in the case of sodium chloride (No. 1). The diffusion coefficient is within the limits of experimental error independent of the concentration gradient excepting for the lowest and highest gradients. In the former case the rather low values may be due to the low amounts diffusing through, with consequent inaccuracies in determination, and in the latter case the large amounts diffusing and thus bringing the real gradient to less than 4·0 and also the noticeable osmotic effects in this case.

From the results (Table II, item 2) given it will be seen that unlike the diffusion of moisture in wood (*vide* Martley, Egner, Narayanamurti) and diffusion of dyestuffs in cellulose (Neale, *et al.*, 1938), the diffusion of salt is independent of the salt concentration as far as sodium chloride is concerned.

To investigate the influence of thickness, the same specimen was used for all the four thicknesses investigated. At the end of the experiment with the largest thickness the specimen was planed down to the next thickness, this procedure being repeated for the other thicknesses. The results (Table II) show the validity of Fick's law.

TABLE II

Sodium Chloride—Effect of Thickness

Species and direction of flow	Thickness cm.	K cm.²/day	
	Effect of thickness		
1 *Canarium strictum* Axial I (10)	1·241, 1·146, 0·958, 0·745	0·349, 0·361, 0·352, 0·392 Mean = 0·363	
	Effect of constant gradient		
	Concentration		
	Higher	Lower	1	2
2 *Canarium strictum* Axial (10)	1·0	0·5	0·458	0·490
	1·5	1·0	0·442	0·430
	2·0	1·5	0·447	0·467
	2·5	2·0	0·465	0·478
			Mean = 0·453	0·466

Christensen obtained a diffusion constant of $3{\cdot}38 \times 10^{-3}$ cm.²/day at 70° F. and $6{\cdot}84 \times 10^{-3}$ cm.²/day at 110° F. for *Eucalyptus obliqua* across

the grain, no results for diffusion along the grain being available. *Salai* (Table I, 2) appears to be less permeable than *Eucalyptus*.

Influence of the type of ion diffusing

The results for copper sulphate axial flow (Table I, 3, 4 and 5) are irregular and show wide variation with different concentration gradients. Whether this is due to precipitation, swelling, adsorption, pH changes, etc., that may be caused, only further experiments can say. In the case of tangential flow the constants agree within 15% in one case and 7% in the other. The variation is higher for radial flow.

The closer agreement for tangential flow may be due to the extremely low permeability of these specimens. The unleached specimen for radial flow, however, shows erratic results, the diffusion constant decreasing with increasing gradient. Possible reaction of the solution with wood constituents may be one of the major causes of this deviation from Fick's law (*vide* Christensen). Stiles (1920, etc.) also found that the diffusion coefficient decreases with concentration of reacting ions in gels.

This is further strengthened by results obtained with cellophane in place of wood. The results are shown in Fig. 3. The constancy of the diffusion coefficient is good. Cellophane is more permeable than *Canarium* across the grain.

The erratic behaviour noticed with potassium dichromate (Table I, 10 to 12) also is possibly due to the reaction and precipitation of chromium.

As can be seen from the results reported, Fick's law is obeyed irrespective of species and direction of flow with arsenic acid (Table I, 13, 14, 15). This is probably due to the fact that unlike copper sulphate and potassium dichromate this substance is not precipitated in wood. The high value of the diffusion coefficient may be due to the high acidity. Christensen's work showed increased diffusion of sodium chloride with decreasing pH. It would be interesting to study the diffusion of H_3AsO_4; or H_2NaAsO_4; Na_2HAsO_4 and Na_3AsO_4 to see the influence of pH.

Ascu

With Ascu (Table III) the tendency of the constant to increase with the concentration can be noticed in the case of copper sulphate and potassium dichromate, even though not to the same extent as with the pure chemicals.

TABLE III

Ascu

Species and direction of flow	Concentration difference in mols./litre w.r.t.			K cm.²/day w.r.t.		
	KCr_2O_7	$CuSO_45H_2O$	$As_2O_52H_2O$	$K_2Cr_2O_7$	$CuSO_45H_2O$	$As_2O_52H_2O$
Cullenia excelsa	0·068	0·06	0·019	0·058	0·056	0·068
Radial (7)	0·136	0·12	0·038	0·112	0·127	0·136
Do II (6)	do	do	do	0·023	0·016	0·025
				0·038	0·035	0·037
Cullenea excelsa	do	do	do	0·0008	Nil	Nil
Tangential I (4)				0·002	Nil	Nil
Do II (5)	do	do	do	0·0015	Nil	Nil
				0·003	0·0025	Nil
Canarium strictum	do	do	do	0·31	0·31	0·31
Axial I (9)				0·47	0·46	0·36
Do II (9)	do	do	do	1·12	1·11	1·41
				1·25	1·35	1·35

Another interesting point to note is that the diffusion constant for the three constituents is almost the same.

Influence of temperature

The results for 3% copper sulphate at three temperatures are given below:

Species and direction of flow	Temperature °C.	K cm²/day	Temperature coefficient 30/20	40/30
Canarium sp.				
Axial I (9)	20, 30, 40	0·327, 0·388, 0·438	1·19	1·13
			Mean = 1·16	
Do II (9)	do	0·176, 0·214, 0·248	1·22	1·16
			Mean = 1·19	
Cullenia excelsa				
Tangential I	do	0·0082, 0·0114, 0·0143	1·39	1·25
			Mean = 1·32	
Do II	do	0·0094, 0·012, 0·015	1·28	1·25
			Mean = 1·27	

As is to be expected, the diffusion constant increases with temperature, the increase being greater with *Cullenia* specimens than with *Canarium* specimens. Christensen found a temperature coefficient of 1·38 for 10° C. for sodium chloride and *Eucalyptus* which was constant between 70° F. and 150° F.

In the present tests there is a slight decrease in the temperature coefficient with rise in temperature, which may be due to the fact that any

reaction of the constituents of wood with copper sulphate is likely to be more, the higher the temperature.

Influence of direction of flow, etc.

The species investigated being hardwoods the longitudinal permeability, as is to be expected, is much more than that across the grain.

Copper sulphate diffuses through *Canarium* in the axial direction several hundred times that in the direction across the grain. The radial permeability is higher than the tangential. Christensen found the radial diffusion to be 2 to 4 times the tangential for some Australian species. With *Cullenia excelsa* the radial permeability is about 5–10 times the tangential permeability for potassium dichromate and 3–4 times for arsenic acid.

In contrast to Christensen, who believes that there is no difference between heartwood and sapwood, our results indicate that specimens near or in the heartwood are less permeable than those running into the sapwood. For example, the diffusion of copper sulphate in the axial direction is several times more in the sapwood (Table I, 3) than in the heartwood (Table I, 4). In the radial and tangential directions also the specimens nearer the heart are more resistant. Similar behaviour is noticeable with potassium dichromate and arsenic acid.

Comparison with the results of other investigators

As earlier remarked, apart from the work of Christensen very little work has been done on the subject. The present results point to the extreme complexity of the problem. While with substances like sodium chloride and arsenic acid, which do not react with the constituents of wood, it is easy to predict the depth of diffusion under definite conditions, it will not be so with various wood preservatives and other chemicals, which chemically undergo transformation in wood. The study of various individual chemicals and mixtures of chemicals may help in the selection of chemicals for diffusion treatments. Work on various organic molecules, resin forming substances, etc., is in progress in this laboratory.

Summary

A simple diffusion cell (which can be easily constructed from perspex sheeting) for studying the passage of molecules, ions, gases, vapours and liquids through wood and other membranes is described.

The diffusion of ions through some species of Indian timbers under variety of conditions has been studied and the results reported.

The results show that the diffusion of ions through wood obeys Fick's law as long as the ion does not react with any constituents of the wood. In other cases there is deviation from this law. The diffusion constant is largest in the axial direction and smallest in the tangential direction. As against other claims, for the species tested, ionic diffusion is higher through sapwood than through heartwood. Temperature increases the rate of diffusion of ions. Diffusion of copper sulphate through cellophane is in conformity with Fick's law and is of the same order as for some timbers.

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RAMAN SPECTRUM OF CANE-SUGAR CRYSTAL

By Roop Kishore and V. M. Padmanabhan

(From the Department of Physics, Indian Institute of Science, Bangalore)

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(Communicated by Prof. R. S. Krishnan, F.A.SC.)

1. Introduction

In view of the interest in the constitution of sugars from organic and biochemical point of view, a study of their Raman spectra is of special importance. In spite of their easy availability, it is surprising to note that very little work has been done on the Raman effect in sugars in the form of crystals. The only investigation reported in the literature is that by Spedding and Stamm (1942). Using the $\lambda 2536$ mercury radiation as exciter they recorded the Raman spectra of α and β glucose both in the form of crystalline powder and in aqueous solutions. Using the same technique, the authors have now investigated the Raman effect in a single crystal of cane-sugar ($C_{12}H_{22}O_{11}$) and also the effect of crystal orientation on the recorded spectrum. The results are described in this paper.

2. Experimental Details

Clear transparent crystals of cane-sugar used in the present investigation were supplied by the Director of the Sugar Technological Institute, Cawnpore. The crystals had their *c* and *a* faces well developed. Specimens with the dimensions $2 \times 1{\cdot}5 \times 1$ cm. were chosen. They were cut and polished so as to get the maximum area for illumination. The crystal was mounted adjacent to the quartz arc which was specially designed to give very intense resonance radiation. Using a Hilger medium quartz spectrograph with a slit width of 0·035 mm., exposures of the order of fifty hours had to be given in order to get intense photographs. It was found that on exposures to the ultra-violet radiations the face of the crystal adjacent to the arc got frosted and thus rendered opaque to the exciting radiation. This disturbing factor was overcome by removing the crystal every hour and repolishing it for further use. Three different spectrograms were photographed corresponding to three different settings of the crystal with respect to the directions of illumination and observation, namely (1) incident light along *a*-axis, scattered light along *c*-axis. (2) incident light along *a*-axis, scattered light along *b*-axis and (3) incident light along *b*-axis and scattered light along *c*-axis.

TABLE I

Cane-Sugar	α-Glucose	β-Glucose
52		
79		
94		
123		
149	142	
167	168	
199		
208		
229	224	
240		
261		
290		
303		
314		
349		
371	363	
	395	
403	405	404
446	441	425
		462
482		
504		523
525		
551	542	
560	580	567
590		580
701		
742		
	774	
851	842	825
867		870
875	887	901
908	913	914
922		
944		941
	1020	1025
1039	1038	
1065	1057	1051
1073	1072	
1104	1109	
1126	1122	1118
		1130
	1149	1151
1161		
1172		
1211	1203	1209
1238	1227	
	1273	1268
	1302	1312
		1336
1347	1345	1350
1366		1363
	1374	1377
1410	1417	
1432		

TABLE I—(*Contd.*)

Cane-Sugar	α-Glucose	β-Glucose
1462	1461	1452
1470		1507
2666	2640	
2724	2700	
	2761	
	2833	
	2856	
2885	2879	2876
2895	2893	2895
		2908
2913	1916	
2929		
2945		
2957		
2973		
2985		2977
2996		
3015		
3342		
3392	3396	
3427		
		3505
3548		3556

RESULTS AND DISCUSSION

An enlarged photograph of the Raman spectrum of cane-sugar and its micro-photometric record is reproduced in Plate (II). Sixty-three Raman lines could be identified and these are tabulated above. The frequency-shifts observed by Spedding and Stamm in the spectra of α- and β-glucose are also included in the same table.

The observed frequency shifts may be broadly classified under two categories: (1) low frequency or lattice lines and (2) internal oscillations of the molecule. Of the eight low frequency lines, the most intense ones are 79 and 94 cm.$^{-1}$ and they are absent in the spectrum of glucose. The probable explanation for the appearance of these two lines is the following. As is well known, cane-sugar is built up of one each of glucose and fructose units. Each glucose unit is bound to a fructose unit loosely by an oxygen atom. The two units are therefore capable of oscillating against each other and the two intense lattice lines may be attributed to these oscillations. The line at 123 cm.$^{-1}$ exhibits marked variation in intensity with the orientation of the crystal and should therefore be assigned to a symmetric class. As the structure of cane-sugar crystals has not been analysed, further analysis of the observed lattice spectrum is not possible at present.

(*b*) (*a*)

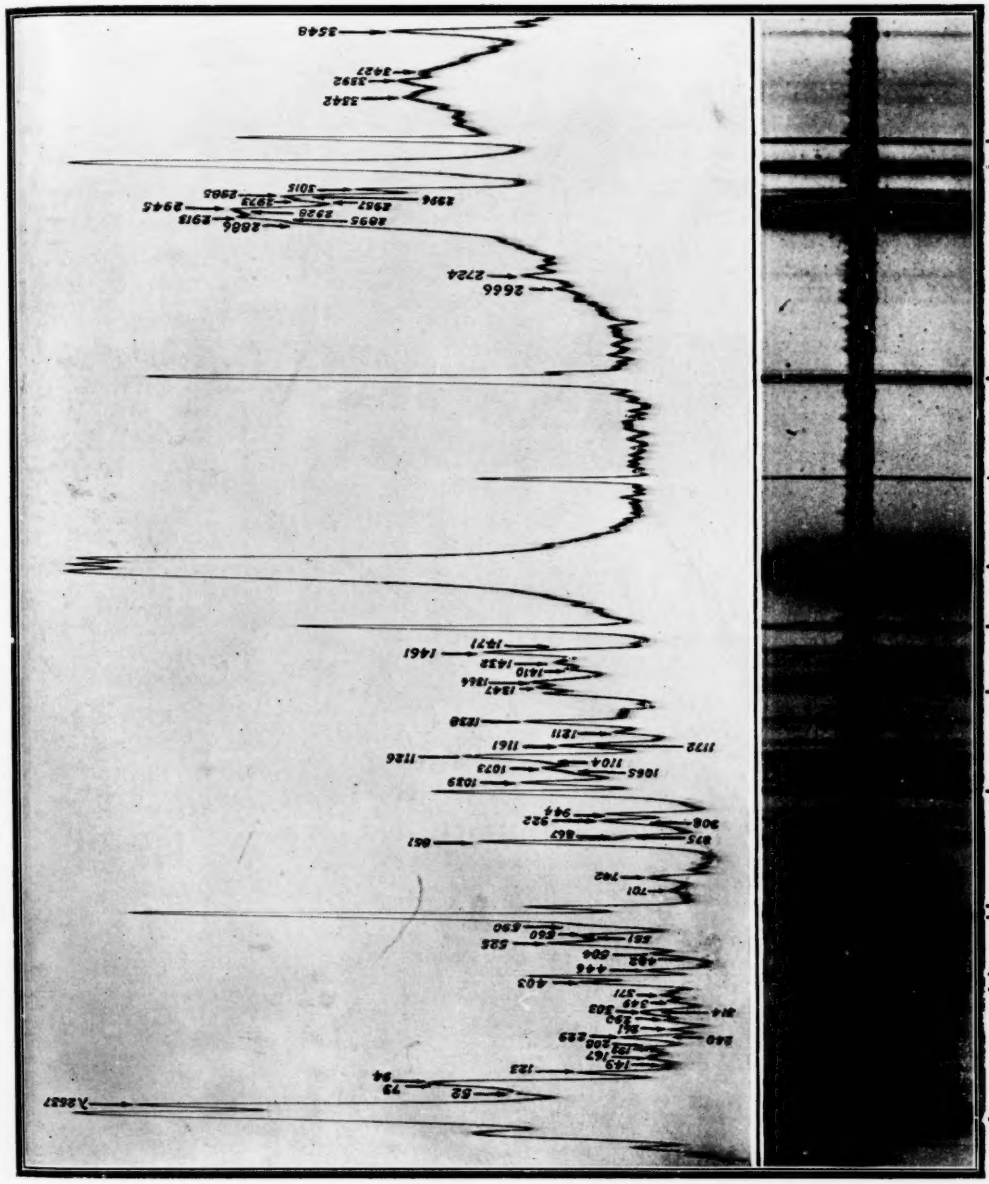

FIG. 1

(*a*) Raman spectrum of cane-sugar crystal
(*b*) Its microphotometer record

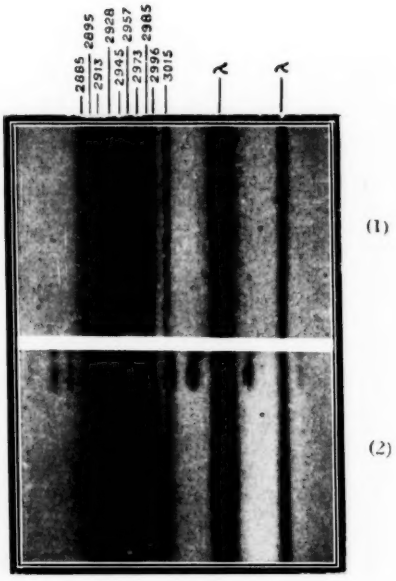

FIG. 2

The spectrum of the C-H oscillations in cane-sugar crystal for two different orientations

Internal frequencies.—As is to be expected, there is a general correspondence between the internal frequencies of the cane-sugar molecule and those of glucose. The most interesting feature of the spectrum is the appearance of a group of ten lines with frequency shifts lying in the range from 2886 cm.$^{-1}$ to 3015 cm.$^{-1}$ These are due to the C-H oscillations. Of these, the lines with frequency shifts 2938, 2973 and 2985 cm.$^{-1}$ are found to exhibit a marked variation in intensity for the two settings of the crystal, namely, (1) incidence along *a*-axis and scattering along *c*-axis and (2) incidence along *a*-axis and scattering along *b*-axis (see Fig. 2). The spectrum obtained for the third orientation was identical with the one taken in the case of (2) stated above. The rest of the lines do not show any variation in intensity. The absence of ketonic or aldehyde groups in the compound is obvious from the non-appearance of any lines in the region 1600–1800 cm.$^{-1}$

The three bands $\approx$ 3342, 3392 and 3427 cm.$^{-1}$ and the intense sharp line at 3427 cm.$^{-1}$ are due to O-H oscillations.

We are grateful to Prof. R. S. Krishnan for guidance and encouragement. Our thanks are also due to the Director of the Sugar Technological Institute, Cawnpore, for kindly presenting the cane-sugar crystals.

Summary

Using λ 2537 mercury resonance radiation as exciter, the Raman spectrum of cane-sugar crystal has been investigated. The recorded spectrum exhibits sixty-three Raman lines. Of these, the two intense Raman lines with frequency shifts 79 and 94 cm.$^{-1}$ which are absent in the spectra of crystals of α- and β-glucose have been attributed to the mutual oscillations of the glucose and fructose units constituting the cane-sugar molecule. The C-H oscillations give rise to a group of ten closely spaced Raman lines.

Reference

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CHEMOTHERAPY OF MALARIA

II. Synthesis of Some Thiazole Derivatives

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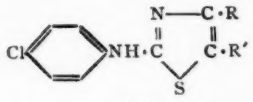
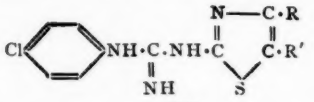
Received April 24, 1951

As indicated in the previous Part,[1] we were interested in tracing the antimalarial activity of compounds of the thiazole group having a simple structure as well as a formal resemblance to the pyrimidine derivatives which led to the development of paludrine in the hands of the British investigators. For this, attempts were made to synthesise compounds of types (I) and (II).



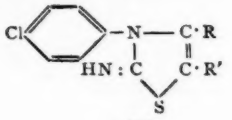
(I)



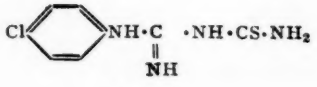
(II)

Compounds of type (I) have been prepared by the standard procedure which consisted in reacting a phenyl (or a naphthyl) thiourea derivative with chloracetal, chloracetone and ethyl α-chloroacetoacetate respectively. The twenty-one thiazole derivatives thus obtained are listed in Table I.

Condensation of the thiourea derivative with the α-halogenoketones can lead to two types of compounds (I) or (II). It has been shown already by Traumann[2] as well as by Hantsch and Weber[3] that only compounds of the type (I) are produced. This has now been confirmed also by the result that the condensation product of *p*-chloroaniline with 2-bromothiazole is identical with the compound obtained by reacting *p*-chlorophenylthiourea with chloracetal.



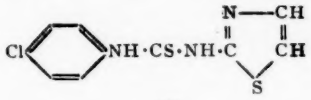
(III)



(IV)

In attempting to evolve a general method of synthesising compounds of formula (II), several methods were tried. The attempts to synthesise the guanidylthioformamide derivative (IV) which could easily be converted into the guanidylthiazoles by reaction with α-chloroketones, ended in failure. Condensation of *p*-chlorophenylcyanamide with thiourea led only to the self-condensation products of the former. Though dicyandiamide has been converted into guanidylthioformamide by the action of hydrogen sulphide,

p-chlorophenylcyanamide could not be converted into the compound (IV) under the standard conditions. The condensation of *p*-chlorophenylcyanamide with 2-aminothiazole did not furnish the guanidylthiazole derivative (II). In view of this, it was not surprising to find that *p*-chlorophenylthiourea and 2-aminothiazole did not react also in the presence of desulphurising agents. However, the guanidylthiazole derivative (II, R = R′ = H) was successfully prepared by desulphurising in the presence of alcoholic ammonia 2-(*p*-chlorophenylthiocarbamido) thiazole (V) itself obtained by the action of *p*-chlorophenylisothiocyanate on 2-aminothiazole. This method appears to be of general applicability and other guanidine derivatives are being prepared.



(V)

The results of testing these compounds for their antimalarial properties will be reported later on.

Experimental

Preparation of thiourea derivatives.—To the amine hydrochloride in alcohol was added potassium thiocyanate (a little over one molecular equivalent) and the mixture refluxed for four hours on the steam-bath. The inorganic salt that separated was filtered off and the filtrate concentrated to dryness. The residue was crystallised from a suitable solvent. The yields of the thiourea derivatives thus obtained were uniformly good. The compounds not reported before are listed in the following table:

Name of Compound	Formula	M. P. °C.	% Nitrogen	
			Found	Required
2-Chlorophenylthiourea	$C_7H_7N_2SCl$	141–3	14·84	15·05
3-Chlorophenylthiourea	$C_7H_7N_2SCl$	137–8	15·42	15·05
2:4-Dichlorophenylthiourea	$C_7H_6N_2SCl_2$	154–6	12·22	12·67
2:5-Dichlorophenylthiourea	$C_7H_6N_2SCl_2$	193–4	12·30	12·67
3:4-Dichlorophenylthiourea	$C_7H_6N_2SCl_2$	198	12·73	12·67

Preparation of thiazole derivatives.—The thiourea derivative taken up in alcohol was treated with the α-halogenoketone or chloracetal (1·1

molecular equivalent) and the mixture refluxed for thirty minutes to four hours, in most cases the reaction being completed in about thirty minutes. The solvent was removed and the residue treated with water and made basic with ammonium hydroxide whereby the thiazole derivative separated. The product was filtered and crystallised from dilute alcohol. The yields of the thiazoles obtained and listed in Table I, are invariably good.

TABLE I

No.	-thiazole	Formula	M. P. °C.	% Nitrogen	
				Found	Required
1	2-*p*-Chloranilino-	$C_9H_8N_2SCl$	167–8	13·66	13·33
2	2-*p*-Chloranilino-4-methyl-	$C_{10}H_9N_2SCl$	146–7	12·42	12·47
3	2-*p*-Chloranilino-4-methyl-5-carbethoxy-	$C_{13}H_{13}N_2O_2SCl$	147–8	9·04	9·44
4	2-*o*-Chloranilino-	$C_9H_8N_2SCl$	92–4	13·66	13·33
5	2-*o*-Chloranilino-4-methyl-	$C_{10}H_9N_2SCl$	70	12·75	12·47
6	2-*o*-Chloranilino-4-methyl-5-carbethoxy-	$C_{13}H_{13}N_2O_2SCl$	99–100	9·57	9·44
7	2-*m*-Chloranilino-	$C_9H_8N_2SCl$	109–11	13·56	13·33
8	2-*m*-Chloranilino-4-methyl-	$C_{10}H_9N_2SCl$	135–6	12·75	12·47
9	2-*m*-Chloranilino-4-methyl-5-carbethoxy-	$C_{13}H_{13}N_2O_2SCl$	145–6	9·26	9·44
10	2-(2′:4′-Dichloranilino)-	$C_9H_6N_2SCl_2$	110–12	10·93	11·43
11	2-(2′:4′-Dichloranilino)-4-methyl-	$C_{10}H_8N_2SCl_2$	132–3	10·88	10·81
12	2-(2′:4′-Dichloranilino)-4-methyl-5-carbethoxy-	$C_{13}H_{12}N_2O_2SCl_2$	139–40	8·29	8·46
13	2-(2′:5′-Dichloranilino)-	$C_9H_6N_2SCl_2$	132–3	11·74	11·43
14	2-(2′:5′-Dichloranilino)-4-methyl-	$C_{10}H_8N_2SCl_2$	183–4	10·95	10·81
15	2-(2′:5′-Dichloranilino)-4-methyl-5-carbethoxy-	$C_{13}H_{12}N_2O_2SCl_2$	112–3	7·95	8·46
16	2-(3′:4′-Dichloranilino)-	$C_9H_6N_2SCl_2$	170	11·33	11·43
17	2-(3′:4′-Dichloranilino)-4-methyl-	$C_{10}H_8N_2SCl_2$	115–6	11·22	10·81
18	2-(3′:4′-Dichloranilino)-4-methyl-5-carbethoxy-	$C_{13}H_{12}N_2O_2SCl_2$	192–3	8·57	8·46
19	2-(4′-Chloro-α-naphthylamino)	$C_{13}H_9N_2SCl$	182–4	10·55	10·76
20	2-(4′-Chloro-α-naphthylamino)-4-methyl-	$C_{14}H_{11}N_2SCl$	158–60	9·8	10·2
21	2-(4′-Chloro-α-naphthylamino)-4-methyl-5-carbethoxy-	$C_{17}H_{15}N_2O_2SCl$	177–8	7·57	8·08

2-p-*Chloroanilinothiazole.*—An intimate mixture of 2-bromothiazole (4 g.) and p-chloraniline (2·5 g.) in phenol medium was maintained for four hours at 150–60° in an oil-bath. The reaction product was cooled and then poured into 5% sodium hydroxide solution. The brown product obtained was filtered and on crystallisation from dilute alcohol it separated in glistening white plates, m.p. 167–8°, which did not show any depression in m.p. on admixture with the thiazole obtained by the reaction of *p*-chlorophenylthiourea with chloracetal.

2-(p-*Chlorophenylthiocarbamido*) *thiazole* (*V*).—*p*-Chlorophenylisothiocyanate (4·2 g.) and 2-aminothiazole (2·5 g.) in benzene (30 c.c.) was refluxed for five hours, the solvent removed and the residue crystallised from dilute alcohol. The thiazole derivative thus obtained (yield 3 g.) had m.p. 185–6° (Found: N, 15·4. $C_{10}H_8N_3S_2Cl$ requires N, 15·58%).

2-(p-*Chlorophenylguanidino*)*thiazole* (*II*, $R = R' = H$).—To the above described thiourea derivative (1·3 g.) in alcoholic ammonia (30 c.c.) was added mercuric oxide (1·1 g.) and the mixture refluxed for five hours. The black precipitate that separated was filtered off, the filtrate concentrated *in vacuo* and the residue crystallised from alcohol to obtain the guanidine derivative (0·8 g.), m.p. 114–5°. (Found: N, 22·49. $C_{10}H_9N_4SCl$ requires N, 22·2%).

Summary

To trace the antimalarial activity in the thiazole compounds, twenty-one thiazole derivatives of general formula I have been synthesised by the standard method of reacting the corresponding thiourea derivatives with chloracetal, chloracetone and ethyl α-chloracetoacetate respectively. The guanidino compound of formula II could not be prepared by the action of *p*-chlorophenylcyanamide on thiourea or by the action of desulphurising agents on a mixture of *p*-chlorophenylthiourea and 2-aminothiazole. *p*-Chlorophenylguanidinothioformamide (IV) could not be prepared by the action of hydrogen sulphide on *p*-chlorophenyldicyandiamide. *p*-Chlorophenylisothiocyanate reacted with 2-aminothiazole to furnish 2-(*p*-chlorophenylthiocarbamido) thiazole (V) which on treatment with mercuric oxide in alcoholic ammonia solution furnished the guanidinothiazole derivative (II).

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ANALYSIS OF SUGARS USING PAPER CHROMATOGRAPHY (HORIZONTAL MIGRATION)

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Paper chromatography has of late become a handy tool in the analysis of mixtures of organic as well as inorganic substances. After its evolution by Consden, *et al.* in 1944,[1] several modifications have been introduced in its technique. An important development in this direction is the Capillary Ascent (Upward Migration) Method of Williams and Kirby,[2] developed in connection with the analysis of amino acid mixtures. The scope of this method has very recently been extended by Rao and Beri[3] for the analysis of sugar mixtures. This method offers some definite advantages over the Downward Migration Method of Consden, *et al.* (*loc. cit.*) in the simplicity of the set-up of the apparatus and the ease of manipulation; yet it takes about 12 to 18 hours for the development of the chromatogram. Recently a modification has been introduced by Rutter[4] into the paper chromatography technique, whereby the substances under analysis are separated into circular zones instead of the usual spots or bands. Amongst the advantages claimed for this method may be mentioned the speed of separation of mixtures, the ease of manipulation and the simplicity and compactness of the apparatus. The suitability of this method for the identification of sugars has now been examined.

The procedure followed is essentially the same as that of Rutter with slight modifications. Whatman No. 1 circular filter-papers have been used for the development of the chromatogram. On irrigation with the solvent mixture the sugar, placed at the centre of the filter-paper, spreads itself into a circular zone of convenient size in about ½ to 2 hours, the size depending on the nature of the solvent, the duration of irrigation and the temperature. The zone is detected by spraying with a suitable reagent. In each case the R_F value (the ratio between the distance through which the solute moves and the distance through which the advancing front of the solvent moves) has been calculated. The values of the different common sugars with different solvents at different temperatures have been determined (Tables I and II). It is clear from the figures in Table I that the values as obtained by the present method are different from those reported by other methods.[3,5] It is, therefore, suggested that these values as determined by the present Horizontal Migration Method be referred to as "Circular R_F Values" to differentiate

them, thereby avoiding confusion, from the values recorded by the Downward or Upward Migration Method, which may be termed "Straight R_F Values".

An examination of the results (Tables I and II) shows that they vary with the solvent used and the temperature maintained, though the latter within close limits does not have a very pronounced effect. It is evident from the values recorded that each sugar has its own characteristic circular R_F value with a particular solvent and a particular temperature so that its identification becomes very easy. Since for Indian laboratories 35° is a convenient temperature which could be maintained conveniently by means of a oven without resort to the low-temperature incubators, the circular R_F values have been determined at 35° with different solvents (Table II). The results show that some of the sugars, though having the same or very close circular R_F values with one solvent, give very much differing values with a different solvent. Further, even if they are present in mixtures, they undergo separation into distinctly different zones, so that they can be identified by determining the circular R_F values in two or more different solvents.

Experimental

General Procedure.—Whatman No. 1 circular filter-paper was used for the development of the chromatogram. Perpendicular to the diameter and at equal distance from the centre two parallel cuts (about 2 mm. apart and 2 cm. in length) were made in the same direction on the filter-paper. The piece lying between the 2 parallel cuts was cut off at the ends away from the centre and folded along the diameter and perpendicular to the plane of the paper (Fig. 1). The " tail " so formed was cut down to about 1·5 cm. in length. For the formation of the "tail" Rutter (*loc. cit.*) used to make parallel cuts from the centre right to the edge. The present method has an advantage over that of Rutter in that the filter-paper retains its firmness, since the rectangular piece cut for the formation of the tail is very small. This facilitates the handling of the filter-paper in subsequent operations with ease and without any deformity. In the formation of the tail it is necessary to see that it is rectangularly perpendicular to the plane of paper, as otherwise the zones may not be truly circular. The sugar solution was placed with the help of a capillary tube as a microdrop (*c*, Fig. 1) on the joint of the tail and the paper, and air-dried. The solvent to be used for the irrigation was taken in a Petri-dish (15 cm. in diameter), and the filter-paper was placed over the dish in such a way that the tail hung down at the centre of the dish, to dip into the solvent below. A glass plate was placed over the filter-paper in order to retard evaporation of the solvent. The whole set-up (Fig. 2) was kept in a thermostat maintained at the required temperature.

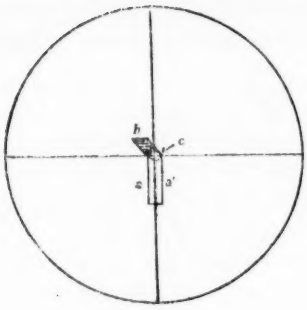

FIG. 1

a and *a'* = Parallel cuts
b = "Tail"
c = Microdrop of the sugar solution

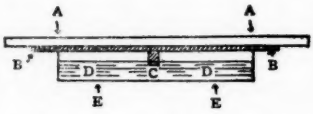

FIG. 2

A = Glass plate
B = Filter paper
C = "Tail"
D = Solvent
E = Petri dish

Through capillary effect the solvent gradually rose from the tail and began to irrigate the filter-paper, uniformly spreading itself in a halo. When the irrigation advanced sufficiently long (10 to 12 cm. in diameter) the paper was removed, placed on another Petri-dish serving as a support and dried in an oven at 105° for 5 minutes, the position of the solvent boundary having been marked with a pencil prior to transfer into the oven. It was then sprayed rapidly and evenly with a solution of aniline hydrogen phthalate in butyl alcohol[6] and dried again at 105° for 5 minutes as before, when a brownish purple zone corresponding to the position taken up by the sugar appeared on an almost white background. From the centre 3 radial lines in 3 different directions were drawn. Along each radial line the distances through which the sugar on the one hand and the solvent on the other moved were measured and the ratio between them was calculated in each case. The average value provided the circular R_F value.

Solvents.—Different solvents were tried for the irrigation:—phenol, *n*-butyl alcohol, *s*-collidine, methyl ethyl ketone, *p*-cresol, *n*-butyric acid and acetophenone. In each case the solvent was saturated with water before its use for the irrigation. Butyric acid and acetophenone were not found suitable, since with anhydrous butyric acid and even water-treated acetophenone, obviously on account of the latter's immiscibility with water, the solutes did not show any movement, while with moist butyric acid the zones were broad and diffused. The other solvents were found to be satisfactory.

Phenol was purified as recommended by Williams and Kirby (*loc. cit.*) by vacuum distillation over zinc dust, and collidine by treatment with bromine

and sodium thiosulphate and final distillation as was done by Partridge.[5] The other solvents were purified by simple distillation under vacuum. A stock solution of phenol was prepared as recommended by Partridge by mixing 100 g. of water with 900 g. of the purified phenol.

Sugar Solutions.—The solutions used were roughly 1 per cent. in concentration except in the case of lactose and maltose wherein a higher concentration was required (about 5 per cent.). In each case 3 to 4 μ l. was taken.

Circular R_F Values of the Common Sugars.—Following the general procedure described above, the circular R_F values were determined at 20° with phenol and at 35° with all the solvents mentioned. For the sake of comparison the straight R_F values as determined by Partridge[5] at 20° are also included in the following table:—

(*a*) *At* 20° *with moist phenol as solvent* (time taken: 2 hours)

TABLE I

	Circular R_F values	Straight R_F values
d-Glucose ..	0·50	0·39
d-Galactose ..	0·54	0·44
d-Mannose ..	0·58	0·45
d-Fructose ..	0·63	0·51
d-Xylose ..	0·58	0·44
d-Arabinose ..	0·64	0·54
l-Rhamnose ..	0·72	0·59
Lactose ..	0·50	0·38
Maltose ..	0·50	0·36

(*b*) *At* 35° *with different solvents.*—With methyl ethyl ketone the development of the chromatogram took about ½ hour, while with the other solvents the time required was 1¼ to 1½ hours.

TABLE II

	Moist phenol	Moist butanol	Moist methyl ethyl ketone	Moist *p*-cresol	Moist *s*-collidine
d-Glucose ..	0·58	0·30	0·22	0·35	0·46
d-Galactose ..	0·60	0·26	0·19	0·37	0·42
d-Mannose ..	0·64	0·32	0·29	0·39	0·53
d-Fructose ..	0·68	0·30	0·30	0·45	0·52
d-Xylose ..	0·62	0·37	0·39	0·39	0·56
d-Arabinose ..	0·68	0·33	0·29	0·49	0·52
l-Rhamnose ..	0·76	0·48	0·47	0·53	0·67
Lactose ..	0·53	0·08	0·13	0·28	0·29
Maltose ..	0·54	0·10	0·15	0·25	0·36

Identification of Sugars, when Present in Mixtures.—Mixed sugar solutions were prepared so that the concentration of the individual sugars was 1 per cent., except in the case of maltose and lactose, where the concentration was maintained at 5 per cent. Their separation into different zones on the chromatogram would naturally depend on the differences in the circular R_F values. From a large number of experiments it was found that a mixture could be separated provided the difference in the R_F values of any 2 components was not less than 0·06. The plate illustrates the separation of the several components of some sugar mixtures into distinct circular zones on running the chromatogram with the suitable solvent. It may be noted that it has not been found possible so far to separate *d*-glucose and *d*-galactose on the chromatogram, the difference in their circular R_F values being less than 0·06 with the different solvents tried.

Summary

Employing filter-paper chromatography a convenient method (Horizontal Migration Method) has been developed for the identification of reducing sugars, when present either alone or in mixtures. Since only small amounts are required for the identification, the method may be useful both to the regular student and the research worker. Under the conditions of the experiment the components of mixtures separate in ½ to 1½ hours into circular zones, which can be easily detected by spraying with a suitable reagent like aniline hydrogen phthalate. Each sugar has its own characteristic circular R_F value (the ratio between the distances through which the sugar moves on the one hand and the solvent front on the other) with a particular solvent, and its determination enables the identification of the sugar. Since some of the sugars have the same or very close R_F values with a particular solvent, it is desirable to run the chromatogram with at least 2 different solvents to confirm the identification. In the case of mixtures it may be necessary to determine the R_F values with 3 or more different solvents in order to definitely identify the individual components. Some of the advantages of the method are the speed and ease of manipulation, simplicity and compactness of the apparatus, and accuracy and reproducibility of the results.

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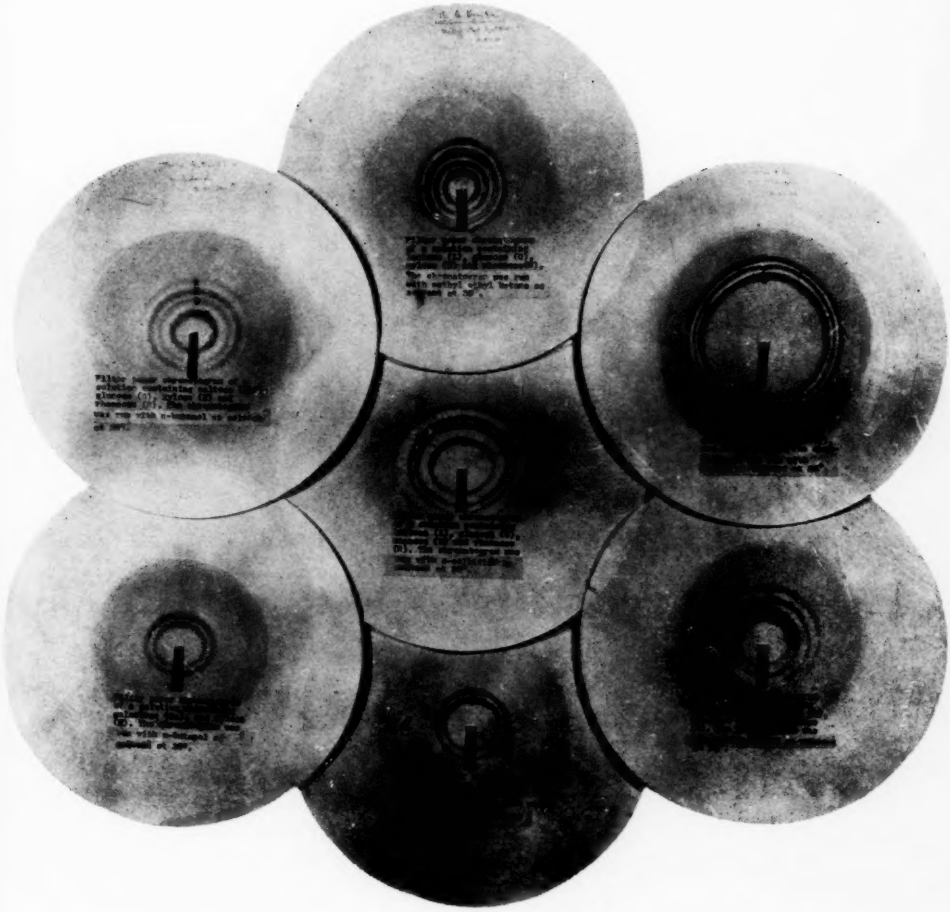

INEQUALITIES CONCERNING BESSEL FUNCTIONS AND ORTHOGONAL POLYNOMIALS

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§1. Introduction

In a paper published sometime ago, Szegö[1] has given several proofs of the following interesting inequality discovered by Turán for Legendre polynomials $P_n(x)$:

$$\Delta_n(x) \equiv P_n^2(x) - P_{n-1}(x)\,P_{n+1}(x) \geqq 0, \qquad n \geqq 1,\ -1 \leqq x \leqq +1 \tag{1.1}$$

Szegö remarks further that inequalities analogous to (1.1) hold also for the ultraspherical, Laguerre and Hermite polynomials. Thus for the ultraspherical polynomials $P_{n,\lambda}(x)$, the analogue of (1.1) reads:

$$\Delta_{n,\lambda}(x) \equiv F_{n,\lambda}^2(x) - F_{n-1,\lambda}(x)\,F_{n+1,\lambda}(x) \geqq 0, \qquad \lambda > -\tfrac{1}{2},\ n \geqq 1,\ -1 \leqq x \leqq +1, \tag{1.2}$$

where $F_{n,\lambda}(x) \equiv P_{n,\lambda}(x) : P_{n,\lambda}(1)$. Subsequently, Madhava Rao and Thiruvenkatachar[2] showed that an elementary proof of (1.1) may be obtained by merely finding $\Delta_n''(x)$, which is given by the elegant formula

$$\Delta_n''(x) = -\frac{2}{n(n+1)}\,P_n'^2(x). \tag{1.3}$$

Similar proofs are also set forth in[2] for the Laguerre and Hermite polynomials $L_n(x)$ and $H_n(x)$. A simple derivation of (1.3) and some other results were given later by one of us.[3] Recently, Szàsz[4] has derived a sharper inequality than (1.2) for $0 < \lambda < 1$:

$$\frac{\lambda\,[1 - F_{n,\lambda}^2(x)]}{(n+\lambda-1)(n+2\lambda)} \leqq \Delta_{n,\lambda}(x) < \frac{n+\lambda}{\lambda+1}\,\frac{\Gamma(n)\,\Gamma(2\lambda+1)}{\Gamma(n+2\lambda+1)} \tag{1.4}$$

which, in the Legendre case ($\lambda = \frac{1}{2}$), reads:

$$\frac{1 - P_n^2(x)}{(2n-1)(n+1)} \leqq \Delta_n(x) < \frac{2n+1}{3n(n+1)}. \tag{1·5}$$

He has also established the following inequality for the Bessel function $J_\nu(x)$:

$$J_\nu^2(x) - J_{\nu-1}(x)\, J_{\nu+1}(x) \geqq \frac{1}{\nu+1}\, J_\nu^2(x), \quad \nu \geqq 0, \ -\infty < x < +\infty. \tag{1·6}$$

The procedure adopted by Szász in deriving (1·4) and (1·6) is based mainly on the respective recurrence relations satisfied by $P_{n,\lambda}(x)$ and $J_\nu(x)$. It has the merit of naturally leading to the more refined inequalities obtained by him, but the results themselves should be capable of a shorter and more direct proof. We illustrate this in this note by utilising the results of [2] and [3] to re-derive the left-hand inequality in (1·5) and, furthermore, to establish the following estimate for $\Delta_n(x)$ which is simpler and more precise than (1·5):

$$\frac{1 - x^2}{2n} \leqq \Delta_n(x) < \frac{2}{\pi n}; \tag{1·7}$$

here the constant $\frac{2}{\pi}$ cannot be replaced by a smaller one. We also set out certain other inequalities which are of interest in this context.

By the same differentiation method, we establish the following interesting inequality analogous to (1·1):

$$J_\nu^2(x) - J_{\nu-1}(x)\, J_{\nu+1}(x) \geqq 0, \qquad \nu \geqq -1, \tag{1·8}$$

from which we readily deduce (1·6) by using the recursion for $J_\nu(x)$. On the other hand, for the modified Bessel function $I_\nu(x)$, we prove the inequality

$$0 \leqq I_\nu^2(x) - I_{\nu-1}(x)\, I_{\nu+1}(x) \leqq \frac{1}{\nu+1}\, I_\nu^2(x), \qquad \nu > -1. \tag{1·9}$$

Finally, we derive some identities whereby the inequality (1·2) for the ultraspherical polynomials, the analogous inequality for the Laguerre polynomials $L_n^{(\alpha)}(x)$ and lastly the inequality (1·6) for Bessel functions are all rendered intuitive. These identities, deduced merely by means of the respective recurrence relations, are analogous to a known identity for Hermite polynomials mentioned by Szàsz in his paper[4] (p. 264). Herewith we secure perhaps the simplest proofs of the inequalities in question.

§2. Legendre Polynomials

We begin by proving the left-hand inequality in (1·5). In fact, we establish a more complete inequality, *viz.*,

$$\Delta_n(x) \gtreqless \frac{1-P_n^2(x)}{(2n-1)(n+1)} \text{ according as } |x| \gtreqless 1 \qquad (n>1). \quad (2.1)$$

To this end, we consider the function

$$f_n(x) = \Delta_n(x) - \frac{1-P_n^2(x)}{(2n-1)(n+1)}, \qquad n>1. \quad (2.2)$$

Differentiating this twice and using (1.3), we obtain on simplification

$$f_n''(x) = \frac{2}{n(n+1)(2n-1)} \{nP_nP_n'' - (n-1)P_n'^2\}.$$

Now we know that the roots of $P_n(x)$ are all real and simple. Denoting them by $x_{\nu n}$ $(\nu = 1, \cdots, n)$, we have

$$\frac{P_n'}{P_n} = \sum_{\nu=1}^{n} \frac{1}{x-x_{\nu n}}, \quad \frac{P_n'^2 - P_nP_n''}{P_n^2} = \sum_{\nu=1}^{n} \frac{1}{(x-x_{\nu n})^2}$$

giving

$$f_n''(x) = \frac{2}{n(n+1)(2n-1)} \left\{\left(\sum_{\nu=1}^{n} P_{\nu n}\right)^2 - n\sum_{\nu=1}^{n} P_{\nu n}^2\right\}, \quad (2.3)$$

where the $P_{\nu n}$ are real polynomials defined by

$$P_n(x) = (x-x_{\nu n})P_{\nu n}(x).$$

Now by Cauchy's inequality, (2.3) gives $f_n''(x) < 0$ so that $f_n'(x)$ is decreasing for all x. Since $f_n(x)$ is an even function, $f_n'(x)$ is an odd function so that $f_n'(0) = 0$. It follows that $f_n'(x) \gtrless 0$ according as $x \lesseqgtr 0$ so that $f_n(x)$ is increasing for $x<0$, decreasing for $x>0$ and has its maximum for $x=0$. Since $f_n(-1) = 0 = f_n(+1)$, (2.1) follows.

Turning to the right-hand inequality in (1.7), we first recall the result which has been obtained in [3] by arguing with $\Delta_n(x)$ on the basis of (1.3) as we have done above with $f_n(x)$ on the basis of (2.3), that $\Delta_n(x)$ has its maximum for $x=0$: $\Delta_n(x) \leqq \Delta_n(0)$ for all x. Now we have

$$n\Delta_n(0) = 2mg_m^2 \ (n = 2m-1 \text{ or } 2m), \text{ with } g_m = \frac{1.3.5\cdots(2m-1)}{2.4.6\cdots 2m}.$$

Since it is easily seen that $mg_m^2 \uparrow \frac{1}{\pi}$ as $m \to \infty$, we find that $n\Delta_n(0) \uparrow \frac{2}{\pi}$ as $n \to \infty$. This establishes the inequality in question as well as the fact that $\frac{2}{\pi}$ is the best possible constant thereof.

To prove the left-hand inequality in (1.7), we make use of the result derived in [3] that the function

$$D_n(x) \equiv P_n'^2(x) - P_{n-1}'(x)P_{n+1}'(x) \quad (2.4)$$

has its minimum for $x=0$ and is connected with $\Delta_n(x)$ by means of the relation

$$n(n+1)\,\Delta_n(x) = (1-x^2)\,D_n(x). \tag{2·5}$$

Herewith we obtain the inequality

$$\Delta_n(x) \gtreqless (1-x^2)\,\Delta_n(0) \text{ according as } |x| \lesseqgtr 1 \quad (n>1). \tag{2·6}$$

Since we have already seen that $n\Delta_n(0)$ is a non-decreasing function of n, we have $n\Delta_n(0) \geqq \Delta_1(0) = \frac{1}{2}$. We now get the inequality in question for $-1 \leqq x \leqq +1$. Note that for $-1<x<+1$, the lower bound for $\Delta_n(x)$ furnished by (1·7) is better than that given by (1·5), the former being $O\left(\frac{1}{n}\right)$ while the latter is $O\left(\frac{1}{n^2}\right)$ since, for $|x|<1$, $P_n^2 \to 0$ as $n \to \infty$.

§3. Bessel Functions

The Bessel function $J_\nu(x)$ of order ν $(-\infty < \nu < +\infty)$ is defined by

$$J_\nu(x) = \sum_{n=0}^{\infty} (-1)^n \frac{c_{\nu,n}}{n!}\left(\frac{x}{2}\right)^{\nu+2n}, \quad c_{\nu,n} = \frac{1}{\Gamma(\nu+n+1)}, \tag{3·1}$$

with the understanding that for $\nu \leqq -1$ we have written

$$c_{\nu,n} = \frac{(\nu+n+1)\cdots(\nu+[-\nu])}{\Gamma(\nu+[-\nu]+1)}, \qquad 0 \leqq n < [-\nu].$$

The modified Bessel function $I_\nu(x)$ is now given by

$$I_\nu(x) = \sum_{n=0}^{\infty} \frac{c_{\nu,n}}{n!}\left(\frac{x}{2}\right)^{\nu+2n}. \tag{3·2}$$

If we write $J_\nu(x) = x^\nu g_\nu(x)$, then $g_\nu(x)$ is an even entire function. It is essential to interpret, in what follows, $J_{\nu-k}\,J_{\nu+k}$ as $(x^2)^\nu\, g_{\nu-k}\, g_{\nu+k}$, with a similar interpretation for $I_{\nu-k}\,I_{\nu+k}$. With this understanding, consider the function

$$\phi_\nu(x) = x^2(J_\nu^2 - J_{\nu-1}\,J_{\nu+1}) \equiv (x^2)^{\nu+1}(g_\nu^2 - g_{\nu-1}\,g_{\nu+1}), \quad \nu \geqq -1, \tag{3·3}$$

which is continuous for all x. Substituting for $J_{\nu-1}$, $J_{\nu+1}$ in terms of J_ν, J'_ν, we have

$$\begin{aligned}\phi_\nu(x) &= x^2 J_\nu^2 - (\nu J_\nu + xJ_\nu')(\nu J_\nu - xJ_\nu') \\ &= (x^2-\nu^2)\,J_\nu^2 + x^2 J_\nu'^2.\end{aligned}$$

Now

$$\begin{aligned}\phi_\nu'(x) &= 2xJ_\nu^2 + 2J_\nu'\{x^2 J_\nu'' + xJ_\nu' + (x^2-\nu^2)\,J_\nu\} \\ &= 2xJ_\nu^2 \equiv 2x\,(x^2)^\nu\, g_\nu^2.\end{aligned}$$

This shows that $\phi_\nu(x)$ is increasing for $x>0$ and decreasing for $x<0$. Since $\phi_\nu(0)=0$, we get $\phi_\nu(x)\geqq 0\ (-\infty<x<+\infty)$ with equality only for $x=0$. This proves (1·8).

Now the recursion formula for the J_ν gives at once

$$\nu J_\nu (J_\nu + J_{\nu+2}) = (\nu+1)\, J_{\nu+1}(J_{\nu-1} + J_{\nu+1}), \tag{3.4}$$

whence, on using the inequality (1·8) just proved, we get

$$\nu J_\nu^2 - (\nu+1)\, J_{\nu-1} J_{\nu+1} = J_{\nu+1}^2 + \nu (J_{\nu+1}^2 - J_\nu J_{\nu+2}) \geqq 0 \qquad (\nu \geqq 0),$$

with equality only for $x=0\ (\nu>0)$. Herewith, Szász's inequality (1·6) is established.

To prove the analogous inequality (1·9) for $I_\nu(x)$, we use the formula

$$I_\lambda(x)\, I_\mu(x) = \sum_{n=0}^{\infty} \binom{\lambda+\mu+2n}{n} c_{\lambda,n}\, c_{\mu,n} \left(\frac{x}{2}\right)^{\lambda+\mu+2n}, \tag{3.5}$$

which one obtains by forming the Cauchy-product of the two absolutely convergent series for I_λ and I_μ. The inequality to be proved now follows from

$$0 < c_{\nu,n}^2 - c_{\nu-1,n}\, c_{\nu+1,n} \leqq \frac{1}{\nu+1}\, c_{\nu,n}^2, \quad \nu > -1,\ n \geqq 0. \tag{3.6}$$

In fact, (3·6) simply amounts to

$$0 < 1 - \frac{\nu+n}{\nu+n+1} \leqq \frac{1}{\nu+1}, \qquad \nu > -1,\ n \geqq 0.$$

The same argument actually proves the following more general inequality:

$$0 \leqq I_{\nu-k+1}(x)\, I_{\nu+k-1}(x) - I_{\nu-k}(x)\, I_{\nu+k}(x) \leqq \frac{2k-1}{\nu+k}\, I_{\nu-k+1}(x)\, I_{\nu+k-1}(x),$$
$$1 \leqq k < \nu+2. \tag{3.7}$$

In particular when ν is a positive integer n, (3·7) easily gives

$$I_0 I_{2n} \leqq I_n^2 \leqq \binom{2n}{n} I_0 I_{2n}. \tag{3.8}$$

§4. Remarks on Turán's Inequality for $P_n(x)$ and Its Analogue for $L_n(x)$

We return for a moment to Turán's inequality (1·1) for the Legendre polynomials $P_n(x)$. For $|x|>1$, the inequality is reversed as has been pointed out in [3]:

$$P_n^2(x) - P_{n-1}(x)\, P_{n+1}(x) < 0, \qquad n \geqq 1,\ |x|>1. \tag{4.1}$$

In this case, we may prove a generalisation of (4·1) analogous to the left-hand inequality in (3·7), *viz.*,

$$P_{n-k+1}(x)\,P_{n+k-1}(x) - P_{n-k}(x)\,P_{n+k}(x) < 0,\ 1 \leqq k \leqq n,\ |x| > 1. \quad (4.2)$$

To prove this, we first observe that

$$P_{n-\nu}(x)\,P_{n+\nu}(x) > 0, \qquad 1 \leqq \nu \leqq n,\ |x| > 1. \quad (4.3)$$

We now use an induction on k and assume (4·2) to hold for some k $(1 \leqq k < n)$. From (4·1) for $n-k$ and $n+k$ respectively, we have

$$P_{n-k}^2\,P_{n+k}^2 < P_{n-k-1}\,P_{n-k+1}\,P_{n+k-1}\,P_{n+k+1}$$
$$< P_{n-k-1}\,P_{n-k}\,P_{n+k}\,P_{n+k+1},$$

by (4·3) and the induction hypothesis. This gives, again by (4·3),

$$P_{n-k}\,P_{n+k} < P_{n-k-1}\,P_{n+k+1},$$

which is (4·2) for $k+1$. Since (4·2) is (4·1) for $k=1$, the proof of (4·2) is complete. For a different proof of (4·2), see [3].

For the Laguerre polynomials $L_n(x)$, the analogue of (1·1) reads:

$$L_n^2(x) - L_{n-1}(x)\,L_{n+1}(x) \geqq 0, \qquad n \geqq 1,\ -\infty < x < +\infty. \quad (4.4)$$

This has been established in [2] for $x \geqq 0$. We shall now extend the argument there given to prove that it holds also for $x < 0$.

From the explicit representation of $L_n(x)$, *viz.*,

$$L_n(x) = \sum_{\nu=0}^{n} \binom{n}{\nu} \frac{(-x)^\nu}{\nu!}, \quad (4.5)$$

it is clear that $L_n(x)$ is an increasing function of n for $x < 0$: we have, in fact,

$$L_n(x) - L_{n-1}(x) = \sum_{\nu=1}^{n} \binom{n-1}{\nu-1} \frac{(-x)^\nu}{\nu!} > 0 \text{ for } x < 0.$$

Hence the function $l_n(x) = e^{-\frac{x}{2}}\,L_n(x)$ introduced in [2] is likewise an increasing function of n for $x < 0$. Now for the function

$$f(x) = l_n^2 - l_{n-1}\,l_{n+1} = e^{-x}\,(L_n^2 - L_{n-1}\,L_{n+1}), \quad (4.6)$$

the following result was derived in [2]:

$$xf'(x) = (l_{n+1} - l_n)\,(l_n - l_{n-1}). \quad (4.7)$$

We therefore have $f'(x) < 0$ for $x < 0$, so that $f(x)$ is decreasing for $x < 0$. Since $f(0) = 0$, it follows that $f(x) > 0$ for $x < 0$. This completes the proof of (4·4).

Since $L_n(x) > 0$ for $x < 0$ as is obvious from (4·5), we get by the inductive argument used for proving (4·2) the analogous inequality:

$$L_{n-k+1}(x)\, L_{n+k-1}(x) - L_{n-k}(x)\, L_{n+k}(x) > 0, \qquad 1 \leqq k \leqq n,\ x < 0. \quad (4\cdot8)$$

§5. Ultraspherical Polynomials

We here generalise part of the results obtained in [3] for the Legendre polynomials to derive upper and lower bounds for $\Delta_{n,\lambda}(x)$ in the case of the ultraspherical polynomials. The results will be found to be analogous to the inequality (2·6).

The ultraspherical polynomials $P_{n,\lambda}(x)$ satisfy the relations

$$(1-x^2)\, P'_{n,\lambda} = (n+2\lambda-1)\, P_{n-1,\lambda} - nxP_{n,\lambda} = (n+2\lambda)\, xP_{n,\lambda} - (n+1)\, P_{n+1,\lambda} \quad (5\cdot1)$$

and the differential equation

$$(1-x^2)\, P''_{n,\lambda} - (2\lambda+1)\, xP'_{n,\lambda} + n(n+2\lambda)\, P_{n,\lambda} = 0. \quad (5\cdot2)$$

If we now recall the definition of $\Delta_{n,\lambda}(x)$ and introduce the numbers

$$k_{n,\lambda} = n(n+2\lambda)\, P_{n,\lambda}^2(1) = (n+2\lambda-1)(n+1)\, P_{n-1,\lambda}(1)\, P_{n+1,\lambda}(1), \quad (5\cdot3)$$

we have

$$k_{n,\lambda}\, \Delta_{n,\lambda}(x) \equiv n(n+2\lambda)\, P_{n,\lambda}^2(x) - (n+2\lambda-1)(n+1)\, P_{n-1,\lambda}(x)\, P_{n+1,\lambda}(x). \quad (5\cdot4)$$

Substituting for $P_{n-1,\lambda}$ and $P_{n+1,\lambda}$ from (5·1), we have

$$k_{n,\lambda}\, \Delta_{n,\lambda} = n(n+2\lambda)\, P_{n,\lambda}^2 - \{nxP_{n,\lambda} + (1-x^2)\, P'_{n,\lambda}\}\{(n+2\lambda)\, xP_{n,\lambda} - (1-x^2)\, P'_{n,\lambda}\}$$
$$= (1-x^2)\,[n(n+2\lambda)\, P_{n,\lambda}^2 + P'_{n,\lambda}\{(1-x^2)\, P'_{n,\lambda} - 2\lambda xP_{n,\lambda}\}]. \quad (5\cdot5)$$

We now introduce the function

$$D_{n,\lambda}(x) \equiv P'^2_{n,\lambda}(x) - P'_{n-1,\lambda}(x)\, P'_{n+1,\lambda}(x). \quad (5\cdot6)$$

Substituting for $P'_{n-1,\lambda}$ and $P'_{n+1,\lambda}$ from the relations

$$P'_{n-1,\lambda} = xP'_{n,\lambda} - nP_{n,\lambda},\ P'_{n+1,\lambda} = xP'_{n,\lambda} + (n+2\lambda)\, P_{n,\lambda}, \quad (5\cdot7)$$

we have

$$D_{n,\lambda} = P'^2_{n,\lambda} - \{xP'_{n,\lambda} - nP_{n,\lambda}\}\{xP'_{n,\lambda} + (n+2\lambda)\, P_{n,\lambda}\}$$
$$= P'_{n,\lambda}\{(1-x^2)\, P'_{n,\lambda} - 2\lambda xP_{n,\lambda}\} + n(n+2\lambda)\, P^2_{n,\lambda}. \quad (5\cdot8)$$

Comparison of (5.5) and (5.8) gives the relation

$$k_{n,\lambda}\,\Delta_{n,\lambda}(x) = (1-x^2)\,D_{n,\lambda}(x). \tag{5.9}$$

Let $n > 1$. Taking derivatives in (5·8) and using (5·2), we have

$$\begin{aligned} D'_{n,\lambda} &= P''_{n,\lambda}\{(1-x^2)\,P'_{n,\lambda} - 2\lambda x P_{n,\lambda}\} + P'_{n,\lambda}\{n(n+2\lambda)\,P_{n,\lambda} \\ &\quad - xP'_{n,\lambda} - 2\lambda P_{n,\lambda}\} \\ &= 2\lambda\,[x\,(P'^{\,2}_{n,\lambda} - P_{n,\lambda}\,P''_{n,\lambda}) - P_{n,\lambda}\,P'_{n,\lambda}]. \end{aligned} \tag{5.10}$$

Now for $\lambda > -\frac{1}{2}$, the roots of $P_{n,\lambda}(x)$ are all real and simple, and lie in $-1 < x < +1$ symmetrically w.r.t. the origin. Denoting them by $x_{\nu n}$ $(\nu = 1, \cdots, n)$, we have

$$\frac{P'_{n,\lambda}}{P_{n,\lambda}} = \sum_{\nu=1}^{n} \frac{1}{x - x_{\nu n}}, \quad \frac{P'^{\,2}_{n,\lambda} - P_{n,\lambda}\,P''_{n,\lambda}}{P^2_{n,\lambda}} = \sum_{\nu=1}^{n} \frac{1}{(x-x_{\nu n})^2},$$

whence (5.10) may be written

$$D'_{n,\lambda} = 2\lambda P^2_{n,\lambda} \sum_{\nu=1}^{n} \left\{ \frac{x}{(x-x_{\nu n})^2} - \frac{1}{x-x_{\nu n}} \right\} = 2\lambda P^2_{n,\lambda} \sum_{\nu=1}^{n} \frac{x}{(x-x_{\nu n})^2}.$$

We now take the roots $x_{\nu n}$ in the form

$$\left.\begin{matrix} -\xi_{\mu n}, +\xi_{\mu n}, \text{ when } n = 2m \\ -\xi_{\mu n}, 0, +\xi_{\mu n}, \text{ when } n = 2m+1 \end{matrix}\right\} \quad (\mu = 1, \cdots, m).$$

Then, in either case, we have

$$D'_{n,\lambda} = 2\lambda P^2_{n,\lambda} \sum_{\mu=1}^{m} \left\{ \frac{\xi_{\mu n}}{(x-\xi_{\mu n})^2} - \frac{\xi_{\mu n}}{(x+\xi_{\mu n})^2} \right\} = 8\lambda x \sum_{\mu=1}^{m} \xi^2_{\mu n} P^2_{\mu n}, \tag{5.11}$$

where the $P_{\mu n}$ are real polynomials defined by

$$P_{n,\lambda}(x) = (x^2 - \xi^2_{\mu n})\,P_{\mu n}(x).$$

From (5.11) we see that

$$\operatorname{sgn} D'_{n,\lambda}(x) = \operatorname{sgn}(\lambda x). \tag{5.12}$$

Remembering $-\frac{1}{2} < \lambda \neq 0$, the following facts concerning the sign of $D_{n,\lambda}(x)$ at 0, $\pm\infty$, ± 1 can be easily established by direct verification:

$$D_{n,\lambda}(0) > 0, \quad D_{n,\lambda}(\pm\infty) = (\operatorname{sgn}\lambda)\cdot\infty, \quad D_{n,\lambda}(\pm 1) > 0. \tag{5.13}$$

By a consideration of the graph of $D_{n,\lambda}(x)$ on the basis of the facts furnished by (5·12) and (5·13), we arrive at the following results:

For $-\frac{1}{2} < \lambda < 0$, $D_{n,\lambda}(x)$ is increasing for $x < 0$, decreasing for $x > 0$ and has its maximum for $x = 0$ resulting in the inequality

$$D_{n,\lambda}(x) > 0 \qquad (-1 \leqq x \leqq +1), \tag{5.14a}$$

which cannot be reversed for $|x| > 1$.

For $\lambda > 0$, $D_{n,\lambda}(x)$ is decreasing for $x < 0$, increasing for $x > 0$ and has its minimum for $x = 0$ resulting in the inequality

$$D_{n,\lambda}(x) > 0, \qquad -\infty < x < +\infty. \tag{5.14b}$$

With (5.14 *a*, *b*), we get (1.2) along with the additional information that *when* $n > 1$, *the inequality* (1.2) *is reversed for* $|x| > 1$ *if and only if* $\lambda > 0$. Moreover, we get the following estimate for $\Delta_{n,\lambda}(x)$ in $-1 \leqq x \leqq +1$:

$$\begin{cases} \dfrac{1-x^2}{1+2\lambda} \leqq \Delta_{n,\lambda}(x) \leqq (1-x^2)\,\Delta_{n,\lambda}(0), & -\frac{1}{2} < \lambda < 0; \\ (1-x^2)\,\Delta_{n,\lambda}(0) \leqq \Delta_{n,\lambda}(x) \leqq \dfrac{1-x^2}{1+2\lambda}, & \lambda > 0. \end{cases} \tag{5.15}$$

This follows immediately, in view of the relation (5.9), from the result obtained above that $D_{n,\lambda}(x)$ for $|x| \leqq 1$ is comprised between

$$D_{n,\lambda}(0) = k_{n,\lambda}\,\Delta_{n,\lambda}(0) \text{ and } D_{n,\lambda}(1) = \frac{k_{n,\lambda}}{1+2\lambda}.$$

§6. Some Identities Yielding Proofs of the Main Inequalities

I. *Ultraspherical polynomials.*—The $F_{n,\lambda}(x)$ introduced in (1.2) satisfy the recursion:

$$(n+2\lambda)\,F_{n+1,\lambda} - 2(n+\lambda)\,xF_{n,\lambda} + nF_{n-1,\lambda} = 0, \qquad n \geqq 1, \tag{6.1}$$

with $F_{0,\lambda} = 1$, $F_{1,\lambda} = x$. Changing n into $n-1$, we have

$$(n+2\lambda-1)\,F_{n,\lambda} - 2(n+\lambda-1)\,xF_{n-1,\lambda} + (n-1)\,F_{n-2,\lambda} = 0, \qquad n \geqq 1, \tag{6.2}$$

with $F_{-1,\lambda} = 0$, $F_{0,\lambda} = 1$. Multiplying (6.2) by $F_{n,\lambda}$, (6.1) by $F_{n-1,\lambda}$ and substituting, we get the relation

$$(n+2\lambda)\,\Delta_{n,\lambda} - (n-1)\,\Delta_{n-1,\lambda} = F_{n-1,\lambda}^2 - 2xF_{n-1,\lambda}\,F_{n,\lambda} + F_{n,\lambda}^2, \quad n \geqq 1, \tag{6.3}$$

with $\Delta_{0,\lambda} = 1$. Since the right member here is evidently non-negative for $|x| \leqq 1$, we get the inequality:

$$(n+2\lambda)\,\Delta_{n,\lambda}(x) \geqq (n-1)\,\Delta_{n-1,\lambda}(x), \qquad n \geqq 1, \; -1 \leqq x \leqq +1. \tag{6.4}$$

This immediately establishes (1.2) for $\lambda > -\frac{1}{2}$ by successive induction, and at the same time yields the more informative estimate:

$$\Delta_{n,\lambda}(x) \geqq \frac{(n-1)!}{(1+2\lambda)\cdots(n+2\lambda)}\,(1-x^2), \; n > 1, \; -1 \leqq x \leqq +1. \tag{6.5}$$

Again, changing n into $n+1$ in (6.3), we have

$$(n+2\lambda+1)\,\Delta_{n+1,\lambda} - n\Delta_{n,\lambda} = F_{n+1,\lambda}^2 - 2xF_{n+1,\lambda}\,F_{n,\lambda} + F_{n,\lambda}^2. \tag{6.6}$$

If we now subtract (6·3) from (6·6) and use the relations [*cf.* (5·1)]

$$(1-x^2)\,F'_{n,\lambda} = n\,(F_{n-1,\lambda} - xF_{n,\lambda}) = (n+2\lambda)\,(xF_{n,\lambda} - F_{n+1,\lambda}), \quad (6\cdot7)$$

we get the relation

$$(n+2\lambda+1)\,\Delta_{n+1,\lambda} - 2\,(n+\lambda)\,\Delta_{n,\lambda} + (n-1)\,\Delta_{n-1,\lambda} = -\frac{4\lambda\,(n+\lambda)}{n^2\,(n+2\lambda)^2}(1-x^2)^2\,F'^2_{n,\lambda}, \quad n \geqq 1. \quad (6\cdot8)$$

Hence the inequality:

$$(n+2\lambda+1)\,(\Delta_{n+1,\lambda} - \Delta_{n,\lambda}) \gtrless (n-1)\,(\Delta_{n,\lambda} - \Delta_{n-1,\lambda}), \; n \geqq 1, \quad (6\cdot9)$$

according as $-\frac{1}{2} < \lambda < 0$ or $\lambda > 0$. This leads us to the additional information that *for all* x, $\Delta_{n,\lambda}(x)$ *is a non-decreasing function of* n *when* $-\frac{1}{2} < \lambda < 0$ *and a non-increasing function of* n *when* $\lambda > 0$.

Consider next the polynomials $P'_{n,\lambda}(x)$. They satisfy the recursion:

$$nP'_{n+1,\lambda} - 2\,(n+\lambda)\,xP'_{n,\lambda} + (n+2\lambda)\,P'_{n-1,\lambda} = 0, \qquad n \geqq 1, \quad (6\cdot10)$$

with $P_{0,\lambda} = 1$, $P_{1,\lambda} = 2\lambda x$. This follows from (5·7).

From (6·10) we can derive the following relation, just as (6·3) was derived from (6·1):

$$nD_{n,\lambda} - (n+2\lambda-1)\,D_{n-1,\lambda} = P'^2_{n-1,\lambda} - 2xP'_{n-1,\lambda}P'_{n,\lambda} + P'^2_{n\lambda}, \qquad n \geqq 1, \quad (6\cdot11)$$

with $D_{0,\lambda} = 0$. We can then derive the following relation from (6·11) by using (5·7), just as (6·8) was derived from (6·3) by using (6·7):

$$(n+1)\,D_{n+1,\lambda} - 2\,(n+\lambda)\,D_{n,\lambda} + (n+2\lambda-1)\,D_{n-1,\lambda} = 4\lambda\,(n+\lambda)\,P^2_{n,\lambda}, \quad n \geqq 0, \quad (6\cdot12)$$

with $D_{-1,\lambda} = D_{0,\lambda} = 0$. From (6·12), it is now easy to deduce the following identity we have in view:

$$g_{n,\lambda}D_{n,\lambda}(x) = 4\lambda \sum_{r=0}^{n-1}\left(\frac{g_{r+1,\lambda}}{r+1} + \frac{g_{r+2,\lambda}}{r+2} + \cdots + \frac{g_{n,\lambda}}{n}\right)(r+\lambda)\,P^2_{r,\lambda}, \quad (6\cdot13)$$

where $g_{n,\lambda} = \dfrac{n!}{2\lambda\,(2\lambda+1)\cdots(2\lambda+n-1)}$ $(n \geqq 1)$.

Herewith, the positivity of $D_{n,\lambda}(x)$ for all x is rendered intuitive when $\lambda > 0$. Furthermore, in view of the relation (5·9), we recover the following complement to (1·2) for $\lambda > 0$:

$$\Delta_{n,\lambda}(x) \gtrless 0 \text{ according as } |x| \lessgtr 1. \quad (6\cdot14)$$

In particular for $\lambda = \frac{1}{2}$ (the Legendre polynomial), we have

$$\Delta_n(x) = \frac{1-x^2}{n(n+1)} \sum_{r=0}^{n-1} \left(\frac{1}{r+1} + \frac{1}{r+2} + \cdots + \frac{1}{n} \right) (2r+1)\, P_r^2. \tag{6.15}$$

We may also mention, without proof, the following identity which serves the same purpose as (6.13):

$$\frac{g_{n,\lambda}}{n+\lambda} D_{n,\lambda}(x) = \lambda \left[\sum_{r=1}^{n-1} (a_{r,\lambda} - a_{r+1,\lambda}) P_{r,\lambda}'^2 + a_{n,\lambda} P_{n,\lambda}'^2 \right], \tag{6.16}$$

with $a_{n,\lambda} = \dfrac{g_{n,\lambda}}{n(n+\lambda-1)(n+\lambda)}$ $(n \geqq 1)$, the $g_{n,\lambda}$ having the same meaning as in (6.13).

II. *Laguerre Polynomials.*—The analogue of Turán's inequality (1.1) for the Laguerre polynomials $L_n^{(\alpha)}(x)$ reads:

$$\Delta_n(x) \equiv (\Lambda_n^{(\alpha)}(x))^2 - \Lambda_{n-1}^{(\alpha)}(x)\, \Lambda_{n+1}^{(\alpha)}(x) \geqq 0, \quad \alpha > -1, \; n \geqq 1, \quad -\infty < x < +\infty, \tag{6.17}$$

where $\Lambda_n^{(\alpha)}(x) \equiv L_n^{(\alpha)}(x) : L_n^{(\alpha)}(0)$. The $\Lambda_n^{(\alpha)}(x)$ defined here satisfy the recursion:

$$(\alpha+n+1)\Lambda_{n+1}^{(\alpha)} - (\alpha+2n+1-x)\Lambda_n^{(\alpha)} + n\Lambda_{n-1}^{(\alpha)} = 0, \quad n \geqq 1, \tag{6.18}$$

with $\Lambda_0^{(\alpha)} = 1$, $\Lambda_1^{(\alpha)} = 1 - \dfrac{x}{\alpha+1}$. Changing n into $n-1$, we have

$$(\alpha+n)\Lambda_n^{(\alpha)} - (\alpha+2n-1-x)\Lambda_{n-1}^{(\alpha)} + (n-1)\Lambda_{n-2}^{(\alpha)} = 0, \quad n \geqq 1, \tag{6.19}$$

with $\Lambda_{-1}^{(\alpha)} = 0$, $\Lambda_0^{(\alpha)} = 1$. Multiplying (6.19) by $\Lambda_n^{(\alpha)}$, (6.18) by $\Lambda_{n-1}^{(\alpha)}$ and subtracting, we get the relation

$$(\alpha+n+1)\,\Delta_n^{(\alpha)} - (n-1)\,\Delta_{n-1}^{(\alpha)} = (\Lambda_n^{(\alpha)} - \Lambda_{n-1}^{(\alpha)})^2, \quad n \geqq 1, \tag{6.20}$$

with $\Delta_0^{(\alpha)} = 1$. This at once leads to the identity:

$$g_n^{(\alpha)}\, \Delta_n^{(\alpha)}(x) = \sum_{\nu=1}^{n} \frac{g_\nu^{(\alpha)}}{\alpha+\nu+1} (\Lambda_\nu^{(\alpha)} - \Lambda_{\nu-1}^{(\alpha)})^2, \tag{6.21}$$

where $g_n^{(\alpha)} = \dfrac{(\alpha+1)\cdots(\alpha+n+1)}{(n-1)!}$ $(n \geqq 1)$. Herewith, (6.17) is made evident. In particular for $\alpha = 0$ [the ordinary Laguerre polynomial $L_n(x)$], we have

$$n(n+1)\,[L_n^2 - L_{n-1} L_{n+1}] = \sum_{\nu=1}^{n} \nu (L_\nu - L_{\nu-1})^2. \tag{6.22}$$

It also appears from (6.20) that (6.17) is true for $-2 < \alpha < -1$ as well,

III. *Bessel functions.*—If we put $\Delta_\nu = J_\nu^2 - J_{\nu-1} J_{\nu+1}$, we can re-write the relation (3·4) already noted for the Bessel function $J_\nu(x)$ in the form

$$(\nu + 1)\,\Delta_\nu - \nu\Delta_{\nu+1} = J_\nu^2 + J_{\nu+1}^2. \tag{6·23}$$

This immediately leads to the relation

$$\frac{\Delta_\nu}{\nu} - \frac{\Delta_{\nu+n}}{\nu+n} = \sum_{r=1}^{n} \frac{J_{\nu+r-1}^2 + J_{\nu+r}^2}{(\nu+r-1)(\nu+r)}. \tag{6·24}$$

Since $J_{\nu+n}(x) \to 0$ as $n \to \infty$, (6·24) yields the following series for Δ_ν:

$$\Delta_\nu = \nu \sum_{n=1}^{\infty} \frac{J_{\nu+n-1}^2 + J_{\nu+n}^2}{(\nu+n-1)(\nu+n)}, \tag{6·25}$$

which is easily seen to be equivalent to

$$J_\nu^2 - J_{\nu-1}J_{\nu+1} = \frac{1}{\nu+1} J_\nu^2 + \frac{2}{\nu+2} J_{\nu+1}^2 + 2\nu \sum_{n=2}^{\infty} \frac{J_{\nu+n}^2}{(\nu+n-1)(\nu+n+1)} \tag{6·26}$$

This series representation of Δ_ν is valid unless ν is a negative integer, in which case it holds with $-\nu$ in place of ν since Δ_ν is an even function of ν for integral values of ν.

For $\nu \geqq 0$, (6·26) at once disposes of Szász's inequality (1·6). It is now significant to note that our inequality (1·8), which asserts the positivity of Δ_ν even for $-1 < \nu < 0$, is not at all placed in evidence by (6·26) like Szász's inequality.

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INDEX TO VOL. XXXIII (A)

AUTHORS' INDEX

Agarwal, H. P. ..	*See* Doss and Agarwal.
Aghoramurthy, K., Narasimhachari, N. and Seshadri, T. R.	Synthetic experiments in the benzopyrone series, XVI, 257.
Bagchi, Hari Das and Mukherjee, Bhola Nath	Note on a pair of functional equations satisfied by $T_n(z)$, 277.
	Note on the mutual relation between the two kinds of Tschebyscheff's functions, 290.
Balakrishna, K. J., Rao, N. Prabhakara and Seshadri, T. R.	Nuclear oxidation in flavones and related compounds, XXXIV, 151.
Balakrishna, K. J., Seshadri, T. R. and Viswanath, G.	A note on 4: 5: 6-trimethoxy-coumaran-3-one, 233.
Beri, R. M. ..	*See* Rao and Beri.
Beri, R. M., Gakhar, K. L. and Rao, P. S.	Nencki's reaction with cresols, 88.
Bhatia, A. B. and Sankaran, T. S.	On the scattering of polarised neutrons by protons, 1.
Chandrasekharan, V. ..	Thermal scattering of light in crystals, III, 183.
..	*See* Ramachandran and Chandrasekharan.
Dikshit, V. K. and Tilak, B. D.	A new synthesis of thiophenes and thiapyrans, V, 78.
Doss, K. S. G. and Agarwal, H. P.	Reduction processes at the dropping mercury electrode in pulsating fields, 66.
Doss, K. S. G. and Kalyanasundaram, A.	Reduction processes at the dropping mercury electrode in pulsating fields, 298.
Fernandes, L. and Ganapathi, K.	Chemotherapy of malaria, II, 364.
Gakhar, K. L. ..	*See* Beri and others.
Ganapathi, K. ..	*See* Fernandes and Ganapathi.
Iyengar, K. S. ..	Temperature dependence of ultrasonic velocity in alcohols, 127.
Iyer, R. N., Shah, K. H. and Venkataraman, K.	Synthetical experiments in the chromone group, XXIV, XXV, 116, 228.

Kalyanasundaram, A. ..	*See* Doss and Kalyanasundaram.
..	Reduction processes at the dropping mercury electrode in pulsating fields: the lead ion, 316.
Kapur, N. S. ..	*See* Singh and Kapur.
Kishore, Roop and Padmanabhan, V. M.	Raman spectrum of cane-sugar crystal, 360.
Krishnamurti, D. ..	Evaluation of the elastic constants of diamond from its Raman frequencies, 325.
Krishnamurti, K. ..	A new adsorption isotherm, 92.
Mukherjee, Bhola Nath ..	*See* Bagchi and Mukherjee.
Nanjundiah, T. S. ..	*See* Thiruvenkatachar and Nanjundiah.
Narasimhachari, N. ..	*See* Aghoramurthy and others.
Narayanamurti, D. and Ratra, R. S.	Diffusion of ions through some Indian timbers, 349.
Narayanan, P. S. ..	Photometry of Raman spectra of crystals, II, 97.
	Raman spectrum of potassium di-hydrogen phosphate, 240.
Nayar, Bal Kishore K. ..	*See* Singh and others.
Neelakantan, S., Rangaswami, S., Seshadri, T. R. and Subramanian, S. Sankara	Chemical investigation of Indian lichens, XI, 142.
Padmanabhan, V. M. ..	*See* Kishore and Padmanabhan.
Pavgi, M. S., Sane, V. C., Sreenivasan, A. and Venkataraman, K.	Sulphanilamides, II, 56.
Prasad, Mata and Sundaram, V.	Syneresis of sodium oleate gels in organic solvents, I, II, III, IV, V, 295, 305, 333, 339, 344.
Radhakrishnan, T. ..	Further studies on the temperature variation of the refractive index of crystals, 22.
Ramachandran, G. N. ..	Theory of optical activity of crystals, I, II, 217, 309.
Ramachandran, G. N. and Chandrasekharan, V.	Photo-elastic constants of sodium chlorate, 199.
Rangachari, P. N. ..	The structure of pectin, 100.
Rangaswami, S. ..	*See* Neelakantan and others.
Rao, N. Prabhakara ..	*See* Balakrishna and others.
Rao, P. S. ..	*See* Beri and others.
Rao, P. S. and Beri, R. M.	Analysis of sugars using paper chromatography (Horizontal migration), 368.

Rao, T. Seshagiri .. Elastic constants of barytes and celestite, 251.

Ratra, R. S. .. *See* Narayanamurti and Ratra.

Row, L. Ramachandra and Seshadri, T. R. Synthetic experiments in the benzopyrone series, XV, 168.

Sane, V. C. .. *See* Pavgi and others.

Sankaran, T. S. .. *See* Bhatia and Sankaran.

Sawhney, P. L., Seshadri, T. R. and Thiruvengadam, T. R. Nuclear oxidation in flavones and related compounds, XXXII, 11.

Seshadri, T. R. .. *See* Aghoramurthy and others.

.. *See* Balakrishna and others.

.. *See* Neelakantan and others.

.. *See* Row and Seshadri.

.. *See* Sawhney and others.

Seshadri, T. R. and Viswanadham, N. Nuclear oxidation in flavones and related compounds, XXXIII, 148.

Shah, K. H. .. *See* Iyer and others.

Shah, N. M. .. *See* Vyas and Shah.

Shanta Kumari, C. .. Raman spectrum of lithium ammonium tartrate monohydrate, 236.

Sharma, S. S. .. Thermal expansion of crystals, VI, VII, 245, 283.

Singh, Bawa Kartar and Kapur, Narinder Singh Studies on the dependence of optical activity on chemical constitution, XXXIV, 42.

Singh, Bawa Kartar, Nayar, Bal Kishore K. and Singh, Kartar The refractive dispersive power of organic compounds, III, 173.

Singh, Kartar .. *See* Singh and others.

Sreenivasan, A. .. *See* Pavgi and others.

Subramanian, S. Sankara *See* Neelakantan and others.

Sundaram, V. .. *See* Prasad and Sundaram.

Sunthankar, A. V. and Tilak, B. D. A new synthesis of thiophenes and thiapyrans, III, 35.

Suryan, G. .. Nuclear resonance in flowing liquids, 107.

Thiruvengadam, T. R. .. *See* Sawhney and others.

Thiruvenkatachar, V. R. and Nanjundiah, T. S. Inequalities concerning Bessel functions and orthogonal polynomials, 373.

Tilak, B. D. .. *See* Sunthankar and Tilak.

.. A new synthesis of thiophenes and thiapyrans, IV, VI, 71, 85.

Tilak, B. D.	..	*See* Dikshit and Tilak.
,,	..	Sulphur isosters of carcinogenic hydrocarbons, I, 131.
Tiwari, Shiva Yogi	..	On the charge independence of nuclear forces, 155.
Vaidya, P. C.	..	The gravitational field of a radiating star, 264.
Venkataraman, K.	..	*See* Pavgi and others.
	..	*See* Iyer and others.
Viswanadham, N.	..	*See* Seshadri and Viswanadham.
Viswanath, G.	..	*See* Balakrishna and others.
Vyas, G. N. and Shah, N. M.		Flavones: a direct synthesis of 6-hydroxy-flavones 112.

TITLE INDEX

Adsorption isotherm, new (Krishnamurti), 92.

Benzopyrone series, synthetic experiments, XV (Row and Seshadri), 168; XVI (Aghoramurthy and others), 257.

Bessel functions and orthogonal polynomials, inequalities concerning (Thiruvenkatachar and Nanjundiah), 373.

Chemotherapy of malaria, II (Fernandes and Ganapathi), 364.

Chromone group, synthetical experiments, XXIV, XXV (Iyer and others), 116, 228.

Diffusion of ions through some Indian timbers (Narayanamurti and Ratra), 349.

Elastic constants of barytes and celestite (Rao), 251.

Elastic constants of diamond, evaluation, from its Raman frequencies (Krishnamurti), 325.

Flavones: a direct synthesis of 6-hydroxy-flavones (Vyas and Shah), 112.

Functional equations satisfied by $T_n(z)$, a pair, note (Bagchi and Mukherjee), 277.

Hydrocarbons, carcinogenic, sulphur isosters, I (Tilak), 131.

Lichens, Indian, chemical investigation, XI (Neelakantan and others), 142.

Nencki's reaction with cresols (Beri and others), 88.

Neutrons, polarised, scattering, by protons (Bhatia and Sankaran), 1.

Nuclear forces, charge independence (Tiwari), 155.

Nuclear oxidation in flavones and related compounds, XXXII (Sawhney and others), 11; XXXIII (Seshadri and Viswanadham), 148; XXXIV (Balakrishna and others), 151.

Nuclear resonance in flowing liquids (Suryan), 107.

Optical activity, dependence, on chemical constitution, studies, XXXIV (Singh and Kapur), 42.

Optical activity of crystals, theory, I, II (Ramachandran), 217, 309.

Organic compounds, the refractive dispersive power, III (Singh and others), 173.

Paper chromatography (horizontal migration), analysis of sugars using (Rao and Beri), 368.

Pectin, the structure (Rangachari), 100.

Radiating star, gravitational field (Vaidya), 264.

Raman spectra of crystals, photometry, II (Narayanan), 97.

Raman spectrum of cane-sugar crystal (Kishore and Padmanabhan), 360.

Raman spectrum of lithium ammonium tartrate monohydrate (Shanta Kumari), 236.

Raman spectrum of potassium di-hydrogen phosphate (Narayanan), 240.

Reduction processes at the dropping mercury electrode in pulsating fields (Doss and Agarwal), 66.

Reduction processes at the dropping mercury electrode in pulsating fields: the nickel ion (Doss and Kalyanasundaram), 298.

Reduction processes at the dropping mercury electrode in pulsating fields: the lead ion (Kalyanasundaram), 316.

Refractive index of crystals, temperature variation, further studies (Radhakrishnan), 22.

Sodium chlorate, photo-elastic constants (Ramachandran and Chandrasekharan), 199.

Sulphanilamides, II (Pavgi and others), 56.

Syneresis of sodium oleate gels in organic solvents I, II, III, IV, V (Prasad and Sundaram), 295, 305, 333, 339, 344.

Thermal expansion of crystals, VI, VII (Sharma), 245, 283.

Thermal scattering of light in crystals, III (Chandrasekharan), 183.

Thiophenes and thiapyrans, a new synthesis, III (Sunthankar and Tilak), 35; IV, VI (Tilak), 71, 85; V (Dikshit and Tilak), 78.

4: 5: 6-trimethoxy-coumaran-3-one, a note (Balakrishna and others), 233.

Tschebyscheff's functions, two kinds, mutual relation between, note (Bagchi and Mukherjee), 290.

Ultrasonic velocity in alcohols, temperature dependence (Iyengar), 127.

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CONTENTS

PAGE

Evaluation of the Elastic Constants of Diamond from Its Raman Frequencies . . . . . D. Krishnamurti 325

Syneresis of Sodium Oleate Gels in Organic Solvents. Part III. Effect of Temperature on the Syneresis of Sodium Oleate Gels in Pinene . . . . . Mata Prasad and V. Sundaram 333

Syneresis of Sodium Oleate Gels in Organic Solvents. Part IV. Effect of Concentration on the Syneresis of Sodium Oleate Gels in Pinene and Xylene . . . . . Mata Prasad and V. Sundaram 339

Syneresis of Sodium Oleate Gels in Organic Solvents. Part V. Syneresis of Sodium Oleate Gels in Mixtures of Organic Solvents . . . . . Mata Prasad and V. Sundaram 344

Diffusion of Ions through Some Indian Timbers . . . . . D. Narayanamurti and R. S. Ratra 349

Raman Spectrum of Cane-Sugar Crystal . . . . . Roop Kishore and V. M. Padmanabhan 360

Chemotherapy of Malaria. II. Synthesis of Some Thiazole Derivatives . . . . . L. Fernandes and K. Ganapathi 364

Analysis of Sugars Using Paper Chromatography (Horizontal Migration) . . . . . P. S. Rao and R. M. Beri 368

Inequalities Concerning Bessel Functions and Orthogonal Polynomials . . . . . V. R. Thiruvenkatachar and T. S. Nanjundiah 373